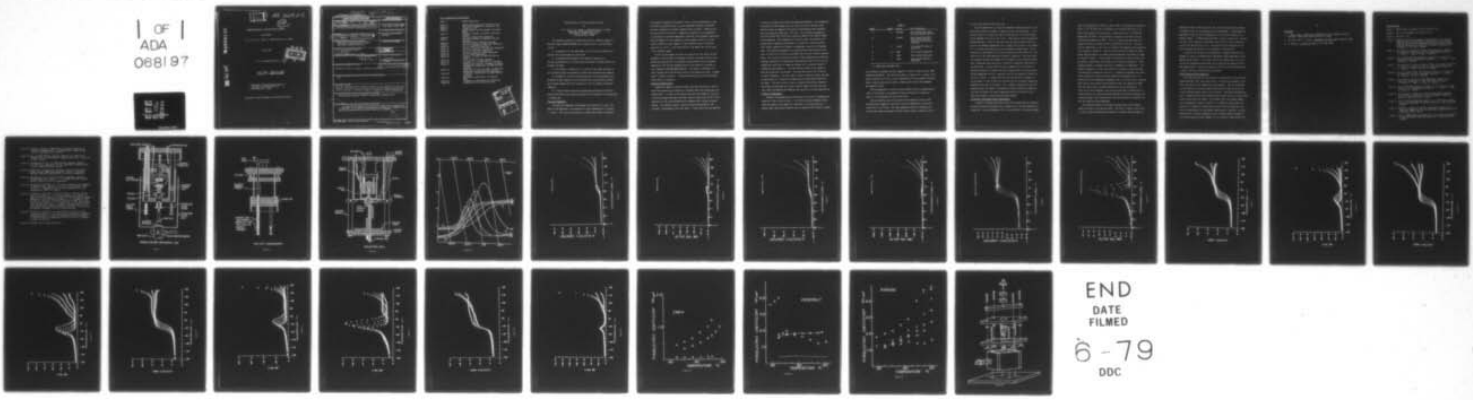
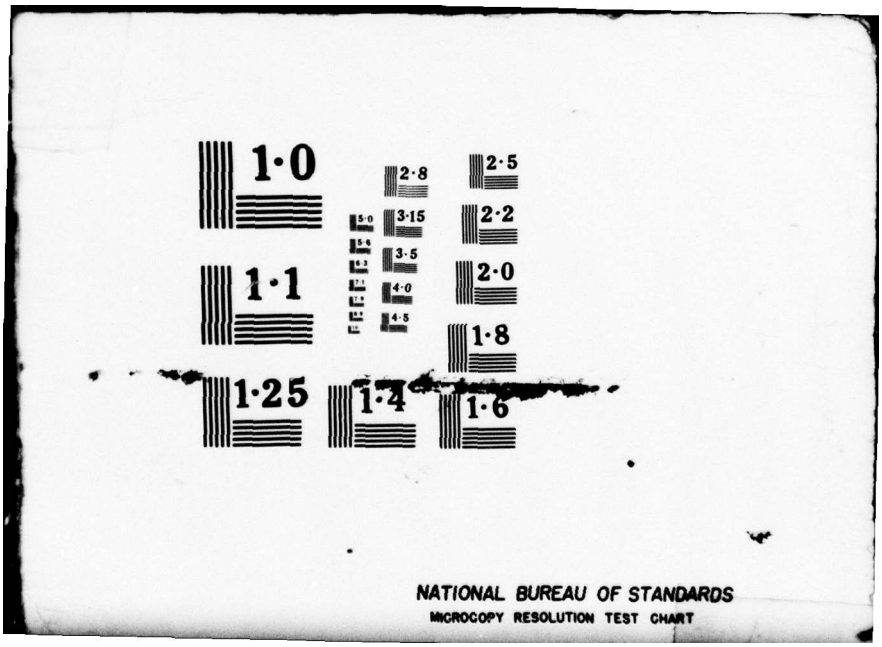
AD-A068 197 CASE WESTERN RESERVE UNIV CLEVELAND OHIO DEPT OF MACR--ETC F/G 11/9
CHARACTERIZATION OF POLYVINYLIDENE FLUORIDE.(U)
MAR 79 M H LITT, J B LANDO, J SCHEINBEIM DAAG29-75-G-0083
UNCLASSIFIED ARO-12659.2-C NL

1 OF 1
ADA
068197



END
DATE
FILMED
6-79
DDC


1·0
1·1
1·25
2·8
3·15
3·5
4·0
4·5
2·5
2·2
2·0
1·8
1·4
1·6
NATIONAL BUREAU OF STANDARDS
MICROCOPY RESOLUTION TEST CHART

LEVEL II

ARO 12659.2-C

(12)

AD A068197

CHARACTERIZATION OF POLYVINYLIDENE FLUORIDE

Final Report

M. H. Litt, J. B. Lando, J. Scheinbeim and J. M. Bates

DDC
RECEIVED
MAY 2 1979
C

March 1979

U. S. Army Research Office

DDC FILE COPY

Grant Number DAAG29 75 G 0083
Proposal No. ~~DAHC04-75G-0083~~

Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

Approved for Public Release; Distribution Unlimited

79 04 30 019

Unclassified (18) ARO (19) 12659.2-C

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER (9) Final Report. Jan 75-Nov 78
2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) (6) Characterization of Polyvinylidene Fluoride,
5. TYPE OF REPORT & PERIOD COVERED: Final Report 1/75-11/78
6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) (10) M. H. Litt, J. B. Lando, J. Scheinbeim, J. M. Bates
8. CONTRACT OR GRANT NUMBER(s): 342-7924

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Macromolecular Science
Case Western Reserve University
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709
12. REPORT DATE (11) Mar 1979
13. NUMBER OF PAGES (12) 36p.

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
15. SECURITY CLASS. (of this report): Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
(15) √DAAG29-75-G-0083
Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)
NA

18. SUPPLEMENTARY NOTES
The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)
Polyvinylidene fluoride, dielectric properties, pyroelectricity

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
An apparatus for measuring the electrical properties of polymer films is described. The dielectric and pyroelectric properties of commercial and radiation polymerized polyvinylidene fluoride are compared.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified 408 357

List of Tables and Illustrations

Table 1.	Sample Preparation.
Figure 1.	Sample holder and can for dielectric cell.
Figure 2.	Gas inlet arrangement for dielectric cell.
Figure 3.	Dielectric cell.
Figure 4.	Sample output from the automatic dielectrometer.
Figure 5.	Dielectric constant of Pennwalt PVF_2 homopolymer.
Figure 6.	Tan δ of Pennwalt PVF_2 homopolymer.
Figure 7.	Dielectric constant of Pennwalt P(VF-VF_2) copolymer.
Figure 8.	Tan δ of Pennwalt P(VF-VF_2) copolymer.
Figure 9.	Dielectric constant of CWRU PVF_2 homopolymer.
Figure 10.	Tan δ of CWRU PVF_2 homopolymer.
Figure 11.	Dielectric constant of Kureha PVF_2 homopolymer.
Figure 12.	Tan δ of Kureha PVF_2 homopolymer.
Figure 13.	Dielectric constant of CWRU homopolymer.
Figure 14.	Tan δ of CWRU homopolymer.
Figure 15.	Dielectric constant of CWRU P(VF-VF_2) copolymer.
Figure 16.	Tan δ of CWRU P(VF-VF_2) copolymer.
Figure 17.	Expanded tan δ of CWRU P(VF-VF_2) copolymer.
Figure 19.	Comparison of dielectric constants of Kureha and CWRU PVF_2 homopolymer and CWRU P(VF-VF_2) copolymer.
Figure 19.	Comparison of tan δ for Kureha and CWRU PVF_2 homopolymer and CWRU P(VF-VF_2) copolymer.
Figure 20.	Pyroelectric coefficients for CWRU P(VF-VF_2) copolymer.
Figure 21.	Pyroelectric coefficients for Pennwalt PVF_2.
Figure 22.	Pyroelectric coefficients for Kureha PVF_2.
Figure 23.	Exploded view of corona poling cell.

79 04 30 019

Characterization of Polyvinylidene Fluoride

by

M. H. Litt, J. B. Lando, J. Scheinbeim and J. M. Bates
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106

The research accomplished through the partial or complete support of ARO grant number DAHC04-75G-0083 can be stated briefly in the following outline.

1) An apparatus for the measurement of the electrical properties of polymer films was designed and constructed.

2) A procedure was developed and an apparatus modified for the bulk polymerization of ultrapure poly(vinylidene fluoride)(referred to hereafter as PVF_2).

3) The dielectric properties of a series of films made from both our own ultrapure polymer and commercial polymer were determined and compared.

4) Pyroelectric current and depolarization current measurements were performed on both samples of our own polymer which we had poled ourselves and on poled samples which were supplied to us by the Kureha and Pennwalt companies.

5) A corona poling device was designed and constructed to allow for better poling than we were able to achieve with the apparatus to be described in section one.

Electrical Apparatus

The electrical apparatus was designed with versatility in mind. The heart of the apparatus is the sample cell, shown schematically in Figures 1, 2 and 3. This cell can be used with a capacitance bridge to determine

the dielectric properties of polymer films or with an electrometer to measure their dc conductivities or current phenomena (thermally stimulated currents, pyroelectric currents, depolarization currents). Sample poling can also be done in this cell. Temperature regulation for the apparatus is provided by a Eurotherm temperature controller and programmer combination. With this sample cell the temperature can be ramped linearly in mV from -196°C to 250°C at rates between 0.1 and 6.25°/min and has a long term stability of ~ 0.1°C. A full description of the sample cell may be found in the 1/77-6/77 report.

As well as the sample cell, which was used for all the electrical measurements to be described in subsequent sections, the grant partially supported the construction of an automatic dielectrometer which can measure sequentially the real and imaginary parts of the dielectric constant at four frequencies (50,500,5000,50,000 Hz). The output is connected to a chart recorder which records both dielectric and temperature data. A sample output is shown in Figure 4. A detailed description of the dielectrometer may be found in reference 1.

Radiation Polymerization

Commercial samples of poly(vinylidene fluoride) were found to contain significant quantities of potentially ionizable impurities grafted onto the polymer chain. In order to distinguish the electrical properties intrinsic to poly(vinylidene fluoride) from those caused by impurities, we felt it was important to find a bulk polymerization procedure which yielded ultrapure polymer. The technique chosen, radiation induced polymerization, was originally investigated by Doll and Lando[2]. A high vacuum rack was modified

to serve as a monomer distillation and degassing apparatus. For homopolymer, vinylidene fluoride monomer was triply distilled into a stainless steel reaction vessel and degassed with several freeze-evacuate-melt sequences. The final pressure at 80°K was $\sim 10^{-5}$ Torr. For P(VF-VF_2) copolymer, 5% triply distilled vinyl fluoride by volume was added to the reaction vessel before degassing. After degassing the reaction vessel was warmed to the polymerization temperature and placed in a cobalt 60 γ radiation source. Sixty percent conversion of monomer to homopolymer required a 0.8 Megarad dose. This technique produced ultra high molecular weight polymer-on the order of three to six million as estimated from intrinsic viscosity measurements. The intrinsic viscosities (dℓ/gm) of PVF_2 homopolymer and P(VF-VF_2) copolymer determined in N,N-dimethyl acetamide were found to be 5.5 and 5.2 respectively while that of commercial polymer with a molecular weight of 140,000 was approximately 1. The high molecular weight of our polymers made them practically intractable. Pressing high quality thin films was virtually impossible. For this reason a study of molecular weight and head to head content as a function of polymerization (temperature) conditions was begun. This work as well as work on reducing the molecular weight of the polymer through addition of chain transfer agents has been continued under ARPA grant DAAK-70-77-C-0055 and the results will be published shortly.

Dielectric Measurements

Dielectric measurements were carried out on the series of homemade and commercial films listed in Table 1. The films were gold shadowed on both sides and placed in the sample cell described in a previous section. A General Radio capacitance bridge was used to determine the dielectric proper-

Table 1

Sample	Phase[a]	Source	Film Preparation
A	II	Pennwalt	Melt pressed from reprecipitated Pennwalt pellets.
B	I	Pennwalt	Melt pressed from Pennwalt pellets coprecipitated with 5% poly(vinyl fluoride).
C	II	Kureha	As received KF capacitor grade film.
D	I,II	CWRU	Melt pressed homopolymer.
E	II	CWRU	Melt pressed homopolymer.
F	I	CWRU	Melt pressed P(VF-VF_2) copolymer.

a. Determined from WAXD scans.

ties (dielectric constant and loss tangent) of films A, B and D at 100, 1000, 10,000 and 100,000 Hz. The results are shown in Figures 5-10. Figures 11-16 show the results for films C, E and F determined with the automatic dielectrometer. Several points can be made in comparing the results from homemade and commercial films.

The low temperature β transition which normally occurs at approximately -70°C at 110 Hz[3] and is attributed the local oscillation of frozen main chains, is not observable for any of the films.

The α_a transition, due to the onset of micro-Brownian motion of the amorphous chain segments at the glass transition temperature, can be seen clearly for all the films. The room temperature dielectric constants for the two films made from Pennwalt pellets (A and B shown in Figures 5 and 7)

are lower than those of the other films.

The high temperature α_c transition produced by molecular motion in the crystalline regions is evident in some but not all of the spectra. It can be seen clearly in Figures 10,14 and 17 which show tan δ for films D and E and an expanded view of tan δ for film F. These are all films of radiation polymerized PVF_2. A hint of the transition can also be found in the tan δ plot for the Pennwalt homopolymer film a (Figure 6) but there is no evidence of it in either the Kureha KF film or the Pennwalt polymer blend. The α_c transition in the commercial films may be obscured by contribution of ionic impurities to the high temperature dielectric properties. Both the dielectric constant and the loss tangent for the Pennwalt films (A and B, Figures 5-8) increase much more rapidly as a function of temperature than those of the other films. Figures 18 and 19 show a comparison of the dielectric properties (dielectric constant and tan δ respectively) for radiation polymerized homopolymer (film E), copolymer (film F) and commercial Kureha film (film C) at 50 Hz. In Figure 18 we see that the dielectric constants of the two phase II films (C and E) are similar and have a greater temperature dependence than that of the phase I film. However, comparison of the loss tangents (Figure 19) shows a considerable difference between the CWRU samples and the Kureha film clearly demonstrating the low levels of ionic impurities present in radiation polymerized samples.

Pyroelectric and Depolarization Measurements

A number of attempts were made to pole films pressed from our radiation polymerized homo and copolymers and to measure their resultant pyroelectric properties. One such homopolymer film, recrystallized in the sample chamber

under a field gradient of 50 KV/cm, gave a small but observable pyroelectric effect ($\sim 10^{-11}$C/°cm^2) while a copolymer film recrystallized under a 120 KV/cm field gradient had a pyroelectric coefficient of 2-3 $\times 10^{-10}$C/°cm^2 between 70° and 120°C. The pyroelectric response of the latter film was unaffected by annealing at 165°C. This is in marked contrast another copolymer film which was poled at 130° and 300 KV/cm for 30 min. The pyroelectric coefficient of this film as a function of temperature and annealing time is shown in Figure 20. Similar curves obtained for samples of experimental PVF_2 provided to us already poled from Pennwalt and Kureha are shown in Figures 21 and 22. It can be seen from these curves that initially the pyroelectric coefficient rises steeply with increasing temperature. After annealing, however, it becomes practically independent of temperature. This behavior suggests to us that the pyroelectric response of poly(vinylidene fluoride) may be composed of two parts: a temperature dependent part which may be annealed out leaving only the temperature independent part. We postulate that the temperature independent part of the pyroelectric response may be due to the classical dipole mechanism while the temperature dependent part may be due to injected charges which may be annealed out. In order to test this hypothesis, work has continued under the ARPA grant to produce films of our radiation polymerized PVF_2 with dipoles aligned by non-electrical means, thus eliminating all possible pyroelectric mechanisms except the classical dipole mechanism.

An interesting effect in the annealing experiment on the Pennwalt sample was noted in last periods report. One sees in Figure 21 that there is a dip in the high temperature pyroelectric response when the sample is

annealed at 129°C for 545 minutes but the current recovers when the sample is allowed to rest at room temperature over the weekend. An experiment was undertaken to map out the time dependence of this current recovery for a Pennwalt sample. It demonstrated that there is also a recovery of a current, like the initial thermally stimulated current, which is lost irreversibly on the first heating after a rest. The results of the experiment are not well understood and more work will be needed to interpret them.

In addition to the work on the pyroelectric response some effort was expended in looking at depolarization phenomena through measurement of the depolarization current. In at least some of the samples there is an indication that spontaneous polarization may be occurring on annealing rather than depolarization. Again this aspect of the work must be pursued farther in order to arrive at more definite conclusions.

Corona Discharge Poling Apparatus

The values observed for the pyroelectric coefficients of the radiation polymerized PVF_2 films, which were poled in the electrical apparatus, were lower than those for the commercially poled samples. This was attributed to the thickness of the melt pressed high molecular weight films and the limited voltage gradient which we could achieve. We, therefore, designed and built a separate corona poling apparatus which would allow us to place higher poling fields across our sample. An exploded view of the sample chamber of this apparatus is shown in Figure 23. A 10,000 volt power supply has been built to supply the voltage across the cell and the progress of the poling is monitored by an electrometer placed across a capacitor in series with the cell. With this apparatus we can routinely achieve voltages of 2-3 million volts per cm for samples of 1 mil capacitor grade Kureha film.

References

1. J. Chiao, Thesis, "Design and Implementation of an Automatic Dielectric Analyzer", Case Western Reserve University (1977).

2. W. W. Doll and J. B. Lando, J. Macromol. Sci.-Phys. B4(4), 897-914 (1970).

3. H. Kakutani, J. Polym. Sci. A2, 8, 1177-1186 (1970).

Figure Captions

Figure 1. Sample holder and sample can for dielectric cell.

Figure 2. Gas inlet arrangement for dielectric cell.

Figure 3. Dielectric cell.

Figure 4. Sample output from the automatic dielectrometer. The real and imaginary parts of the dielectric constant (ε' and ε'' respectively) for four different measurement frequencies (50 Hz, 500 Hz, 5 KHz and 50 KHz) and the output of the sample thermocouple are recorded on a strip chart recorder.

Figure 5. The dielectric constant of Pennwalt PVF_2 homopolymer (sample A) as a function of temperature for four measurement frequencies: 1. 100 Hz, 2. 1 KHz, 3. 10 KHz, 4. 100 KHz.

Figure 6. Tan δ of Pennwalt PVF_2 homopolymer (sample A) as a function of temperature at four measurement frequencies: 1. 100 Hz, 2. 1 KHz, 3. 10 KHz, 4. 100 KHz.

Figure 7. The dielectric constant of Pennwalt $P(VF_2- VF)$ copolymer (sample B) as a function of temperature for four measurement frequencies: 1. 100 Hz, 2. 1 KHz, 3. 10 KHz, 4. 100 KHz.

Figure 8. Tan δ of Pennwalt $P(VF_2- VF)$ copolymer (sample B) as a function of temperature for four measurement frequencies: 1. 100 Hz, 2. 1 KHz, 3. 10 KHz, 4. 100 KHz.

Figure 9. The dielectric constant of CWRU homopolymer (sample D) as a function of temperature for four measurement frequencies: 1. 100 Hz, 2. 1 KHz, 3. 10 KHz, 4. 100 KHz.

Figure 10. Tan δ of CWRU PVF_2 homopolymer (sample D) as a function of temperature for four measurement frequencies: 1. 100 Hz, 2. 1 KHz, 3. 10 KHz, 4. 100 KHz.

Figure 11. The dielectric constant of Kureha PVF_2 homopolymer (sample C) as a function of temperature at four measurement frequencies: ◘ 50 Hz, + 500 Hz, ◆ 5 KHz, x 50 KHz.

Figure 12. Tan δ of Kureha homopolymer (sample C) as a function of temperature at four measurement frequencies: ◘ 50 Hz, + 500 Hz, ◆ 5 KHz, x 50 KHz.

Figure 13. Dielectric constant of CWRU PVF_2 homopolymer (sample E) as a function of temperature for four measurement frequencies: ◘ 50 Hz, + 500 Hz, ◆ 5 KHz, x 50 KHz.

Figure 14. Tan δ of CWRU homopolymer (sample E) as a function of temperature at four measurement frequencies: ◘ 50 KHz, + 500 Hz, ◆ 5 KHz, x 50 KHz.

Figure 15. Dielectric constant of CWRU P(VF-VF_2) copolymer (sample F) as a function of temperature for four measurement frequencies: □ 50 Hz, + 500 Hz, ◇ 5 KHz, x 50 KHz.

Figure 16. Tan δ of CWRU P(VF-VF_2) copolymer (sample F) as a function of temperature for four measurement frequencies: □ 50 Hz, + 500 Hz, ◇ 5 KHz, x 50 KHz.

Figure 17. Expanded view of tan δ for CWRU P(VF-VF_2) copolymer (sample F) as a function of temperature for four measurement frequencies: □ 50 Hz, + 500 Hz, ◇ 5 KHz, x 50 KHz.

Figure 18. Comparison of the dielectric constants at 50 Hz of Kureha homopolymer (sample C) □, CWRU homopolymer (sample E) +, and CWRU P(VF-VF_2) copolymer (sample F) ◇ as a function of temperature.

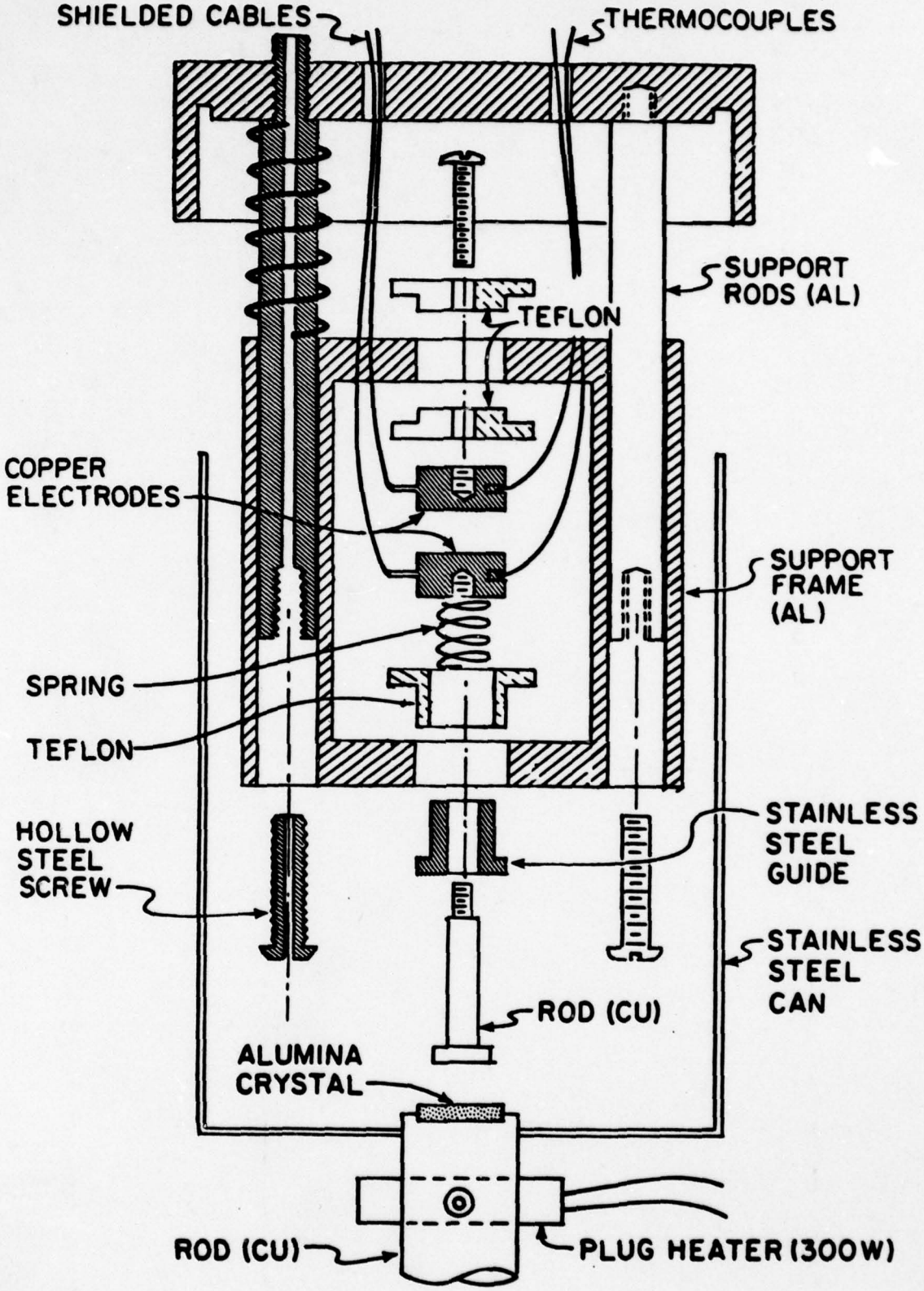
Figure 19. Comparison of tan δ at 50 Hz for Kureha homopolymer (sample C)-□, CWRU homopolymer (sample E) - +, and CWRU P(VF-VF_2) copolymer (sample F)-◇ as a function of temperature.

Figure 20. Pyroelectric coefficient as a function of temperature and annealing for CWRU P(VF-VF_2) copolymer: o initial run, □ annealed at 129°C for 50 min., Δ annealed at 129°C for approximately 80 min. and subsequently at 160°C for 1300 min.

Figure 21. Pyroelectric coefficient for Pennwalt PVF_2 as a function of temperature and annealing: o initial run (sample 1), □ annealed at 129°C for 60 min. (sample 1), Δ annealed at 129°C for 390 min (sample 1), ◇ annealed at 129°C for 645 min (sample 1). ---- annealed at 129°C for 545 min, room temp. for 60 hours and then at 129°C for an additional 45 min (sample 1), -•-•-•- annealed at 125° for 2470 min and 160°C for 4260 min (sample 2). Sample 2 showed substantially the same behavior after an additional 4250 min at 160°C. No correction was made for shrinkage of the film during annealing.

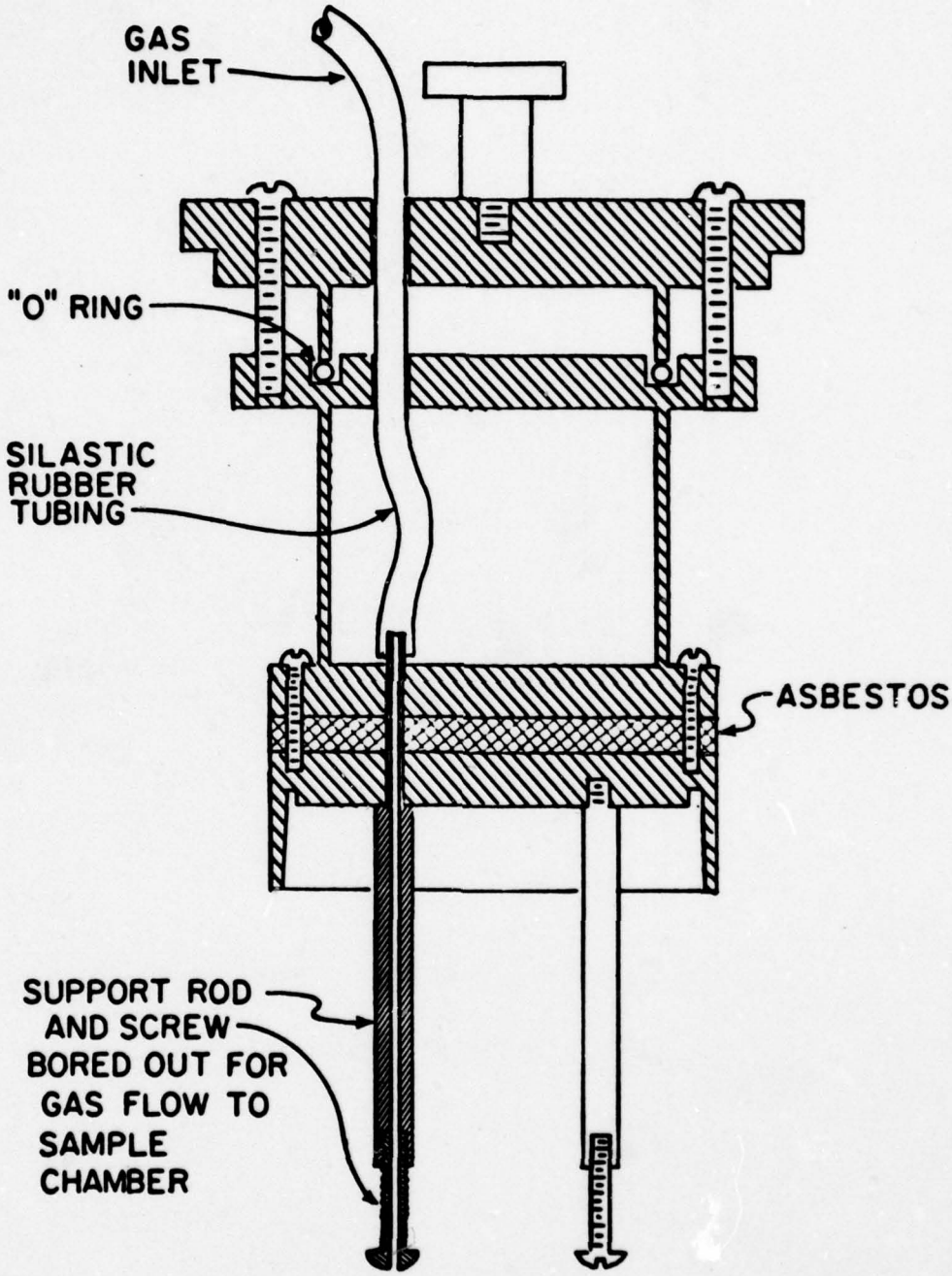
Figure 22. Pyroelectric coefficient for Kureha PVF_2 as a function of temperature and annealing: o as received film uncorrected for thermally stimulated current, x initial run corrected for TSC., ◆ annealed at 132°C for 65 min., □ annealed at 132°C for 170 min., Δ annealed at 132°C for 1170 min.

Figure 23. Exploded view of corona poling cell.



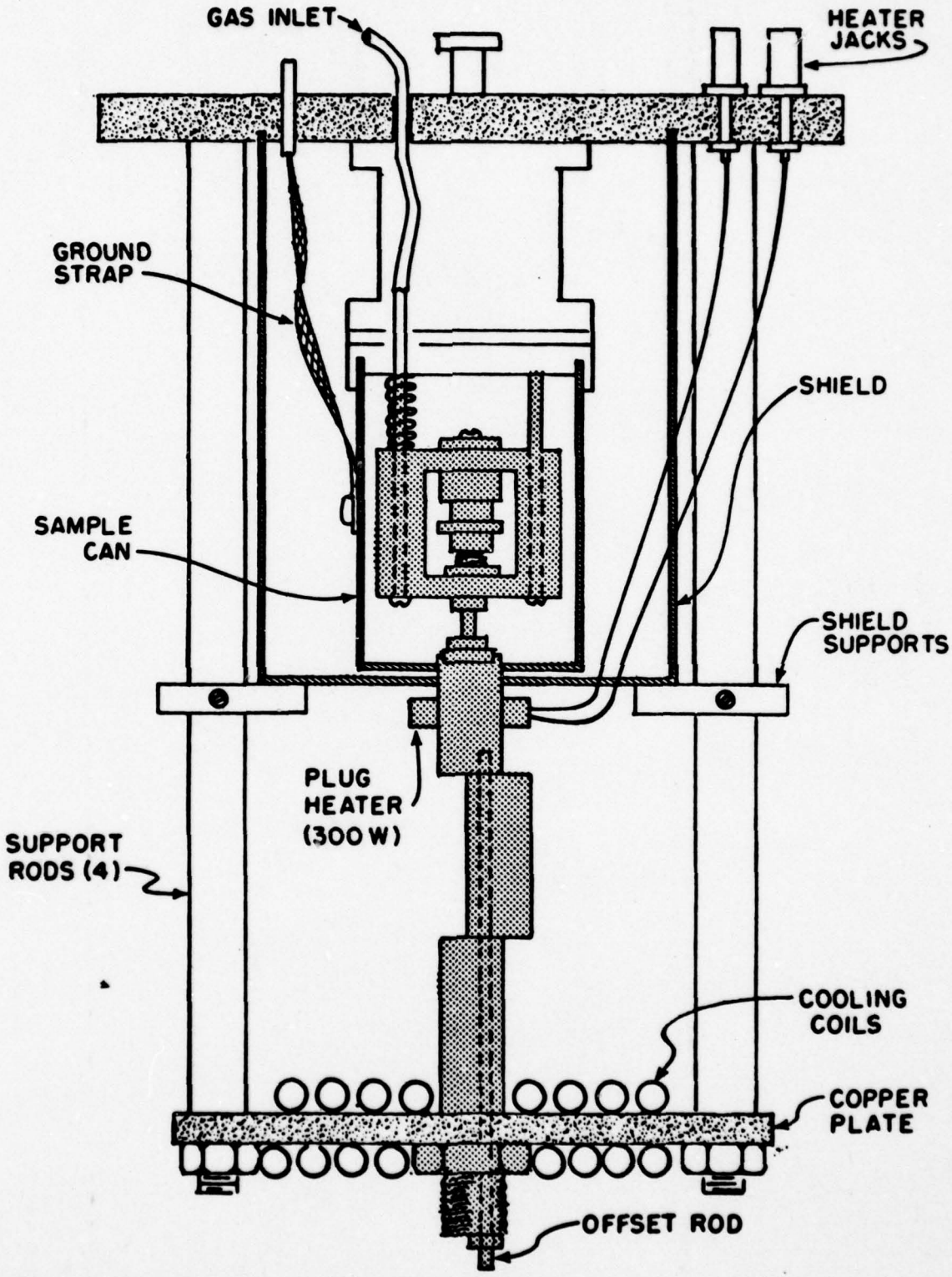
SAMPLE HOLDER AND SAMPLE CAN

Figure 1.



GAS INLET ARRANGEMENT

Figure 2.



DIELECTRIC CELL

Figure 3.

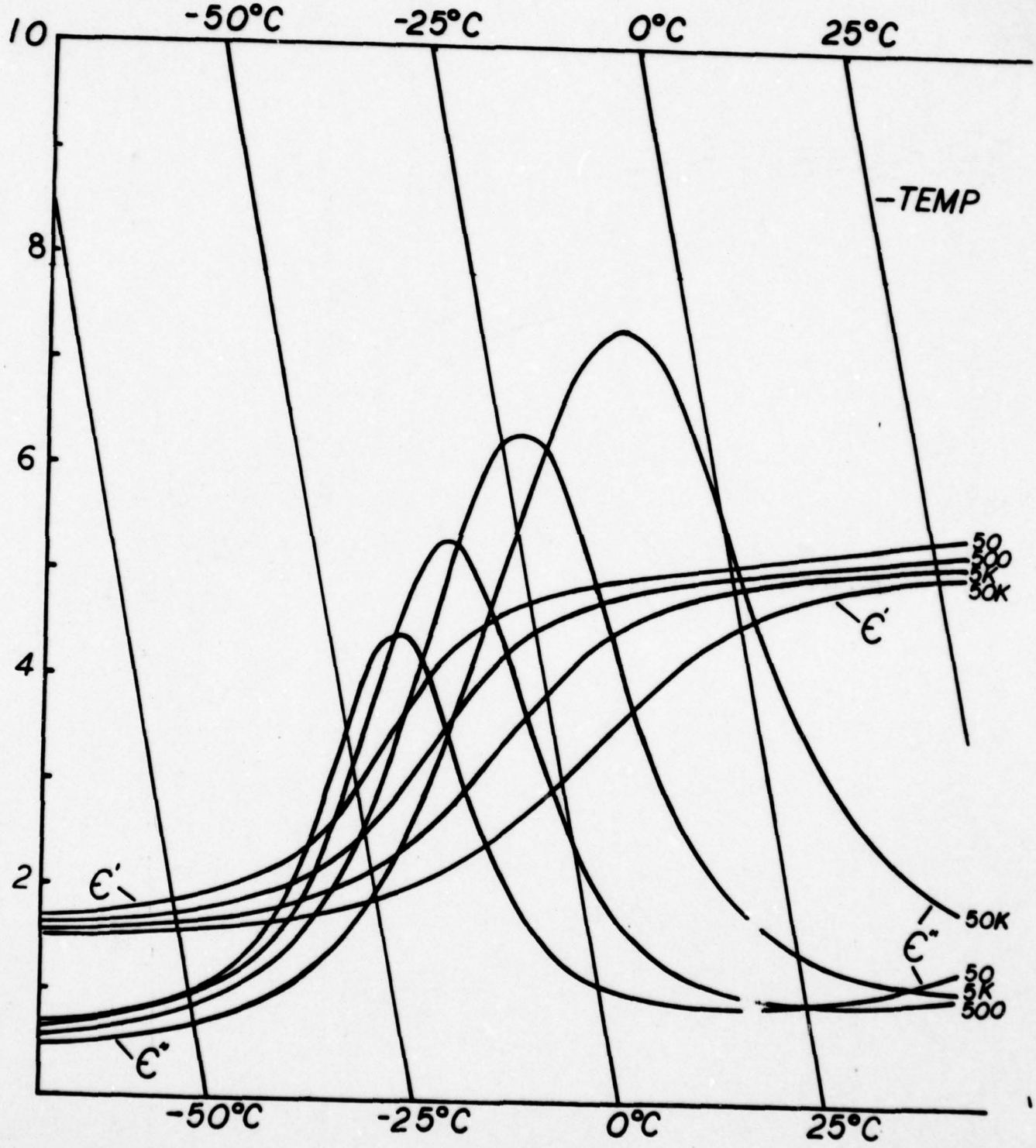

10
8
6
4
2
-50°C
-25°C
0°C
25°C
-TEMP
50
500
5K
50K
ε'
ε''
50K
50
5K
500
-50°C
-25°C
0°C
25°C

Figure 4.

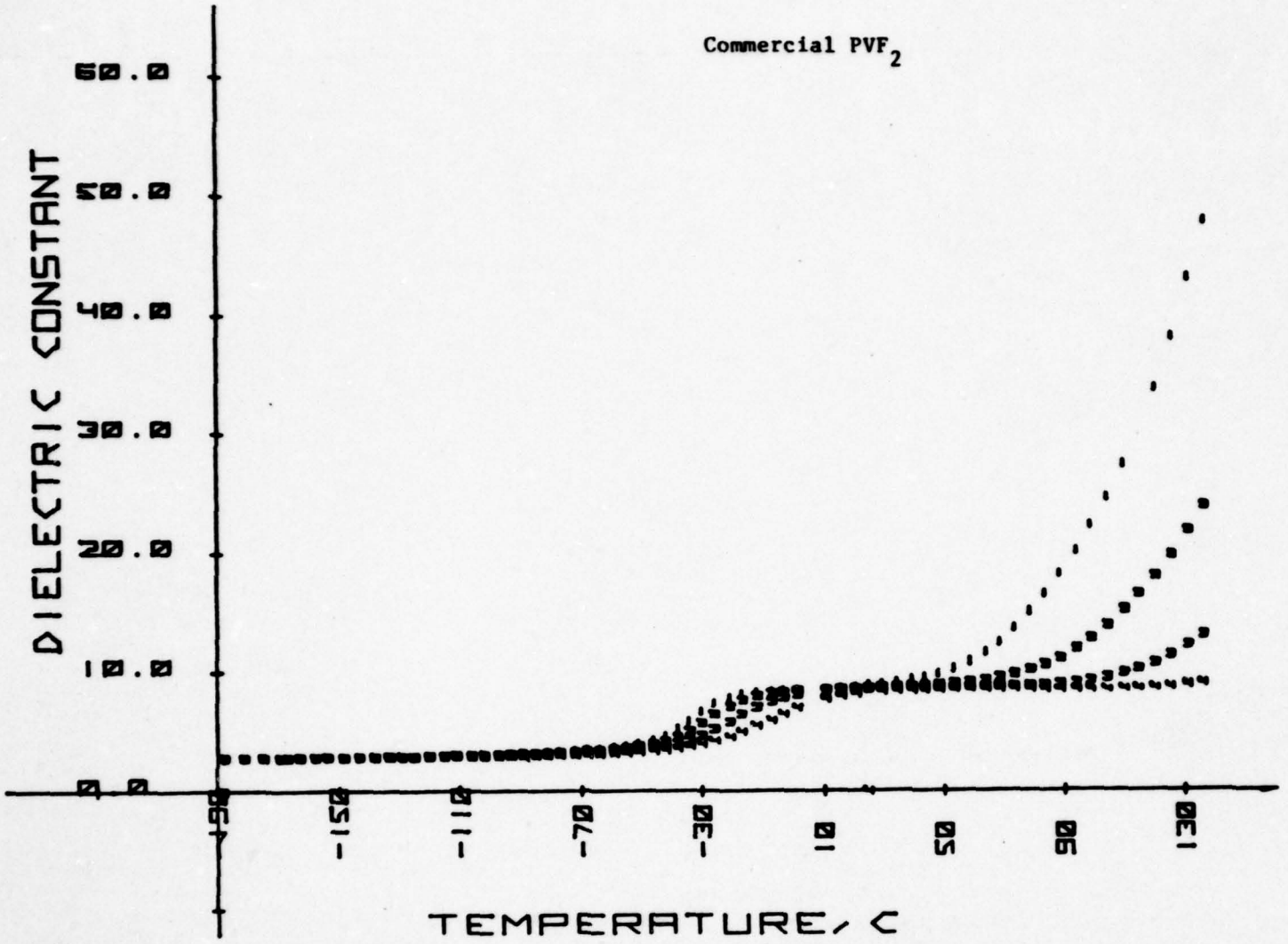

Commercial PVF2
DIELECTRIC CONSTANT
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0
-190
-150
-110
-70
-30
10
50
90
130
TEMPERATURE, C

Figure 5.

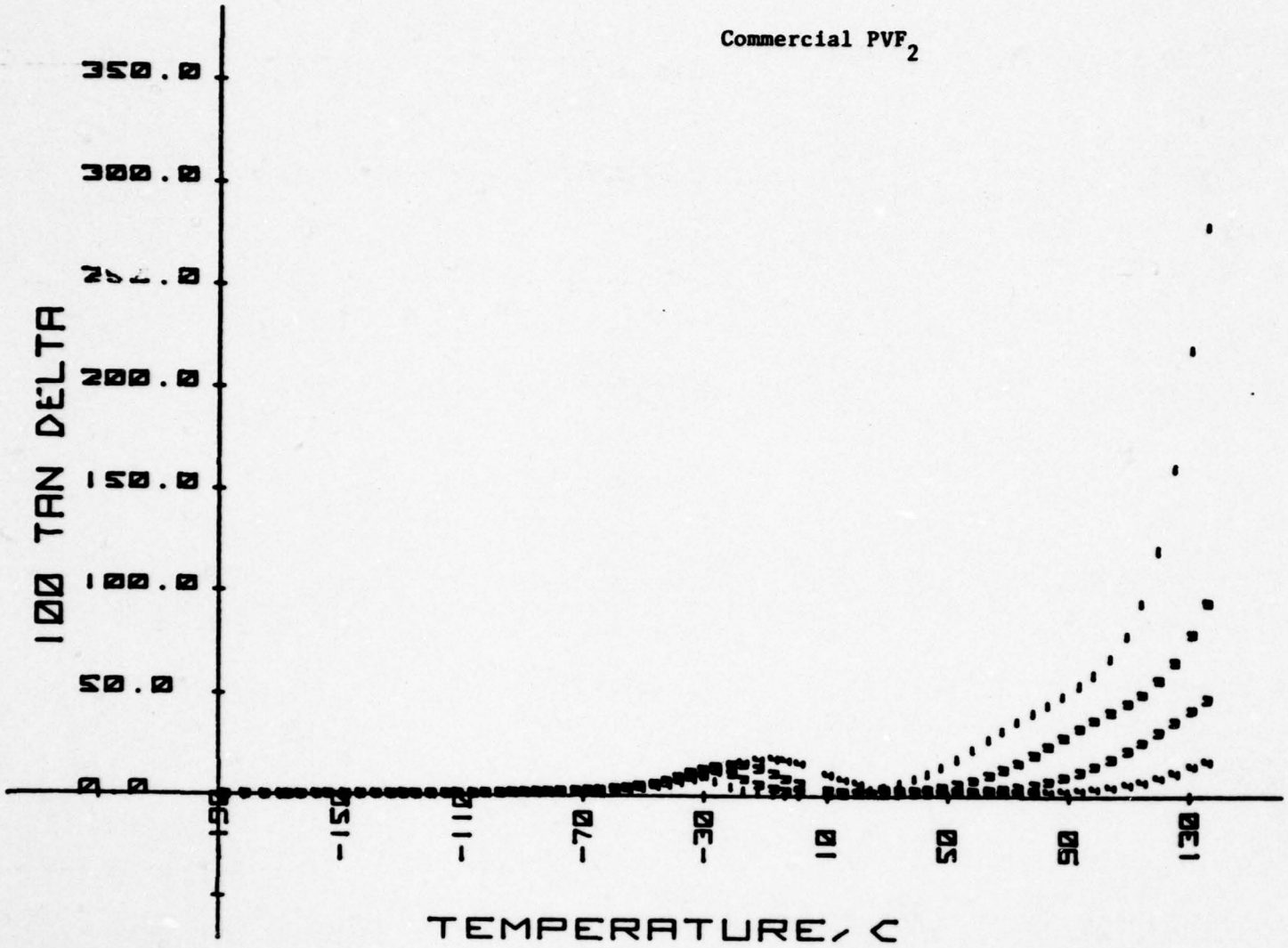

Commercial PVF2
100 TAN DELTA
350.0
300.0
250.0
200.0
150.0
100.0
50.0
0.0
-190
-150
-110
-70
-30
10
50
90
130
TEMPERATURE, C

Figure 6.

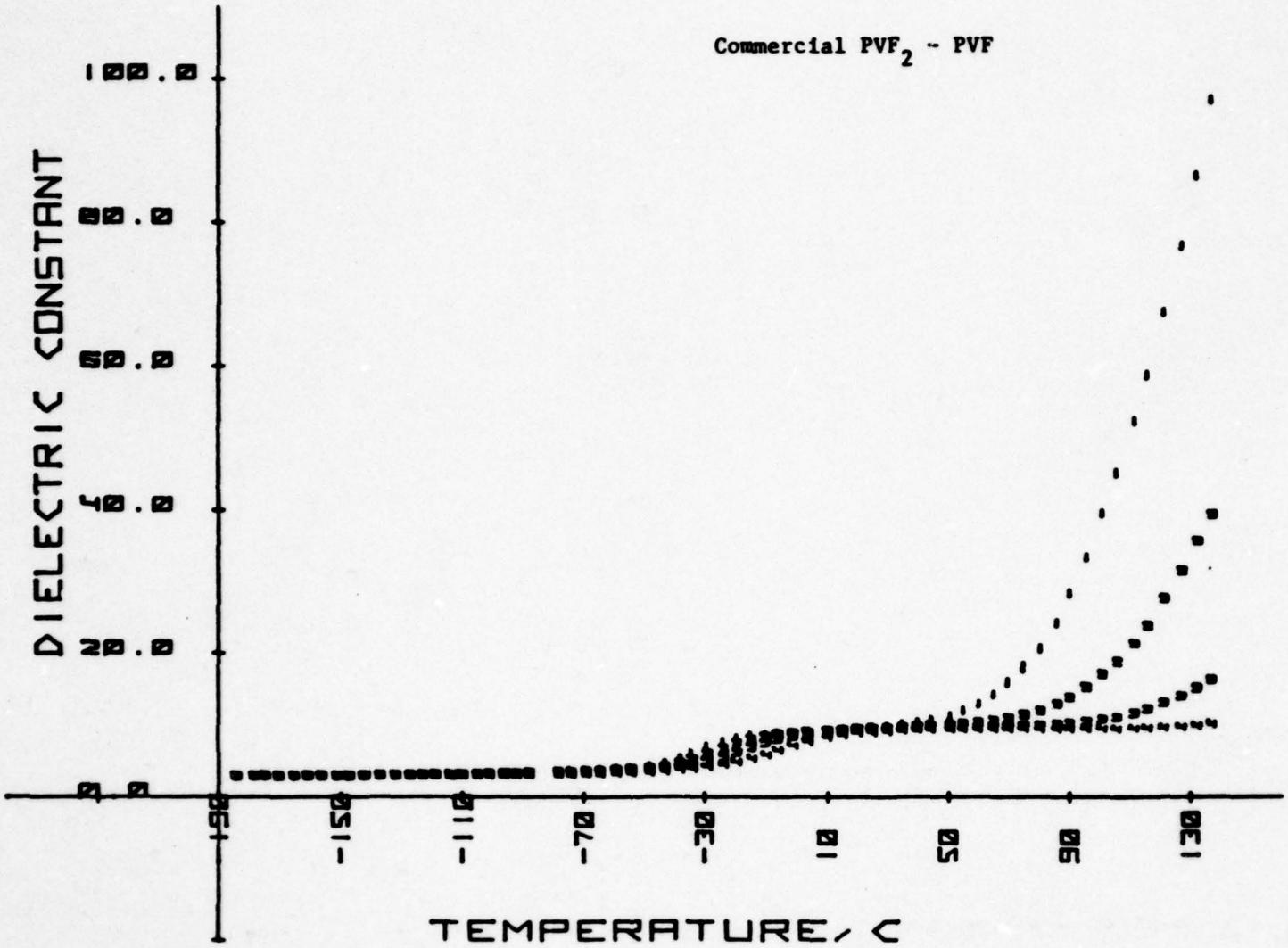

Commercial PVF2 - PVF
DIELECTRIC CONSTANT
100.0
80.0
60.0
40.0
20.0
0.0
-190
-150
-110
-70
-30
10
50
90
130
TEMPERATURE, C

Figure 7.

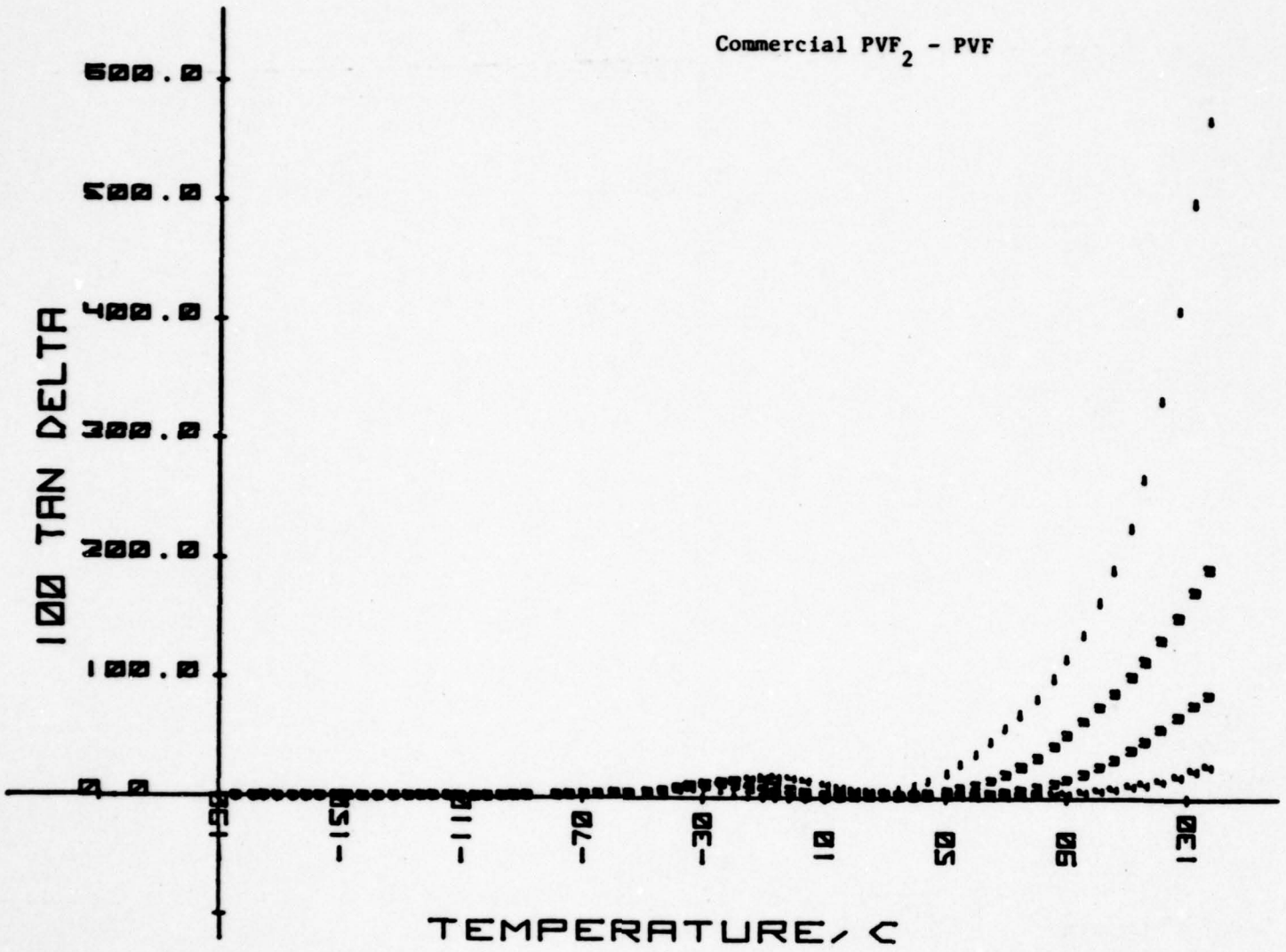

Commercial PVF2 - PVF
100 TAN DELTA
600.0
500.0
400.0
300.0
200.0
100.0
0.0
-190
-150
-110
-70
-30
10
50
90
130
TEMPERATURE, C

Figure 8.

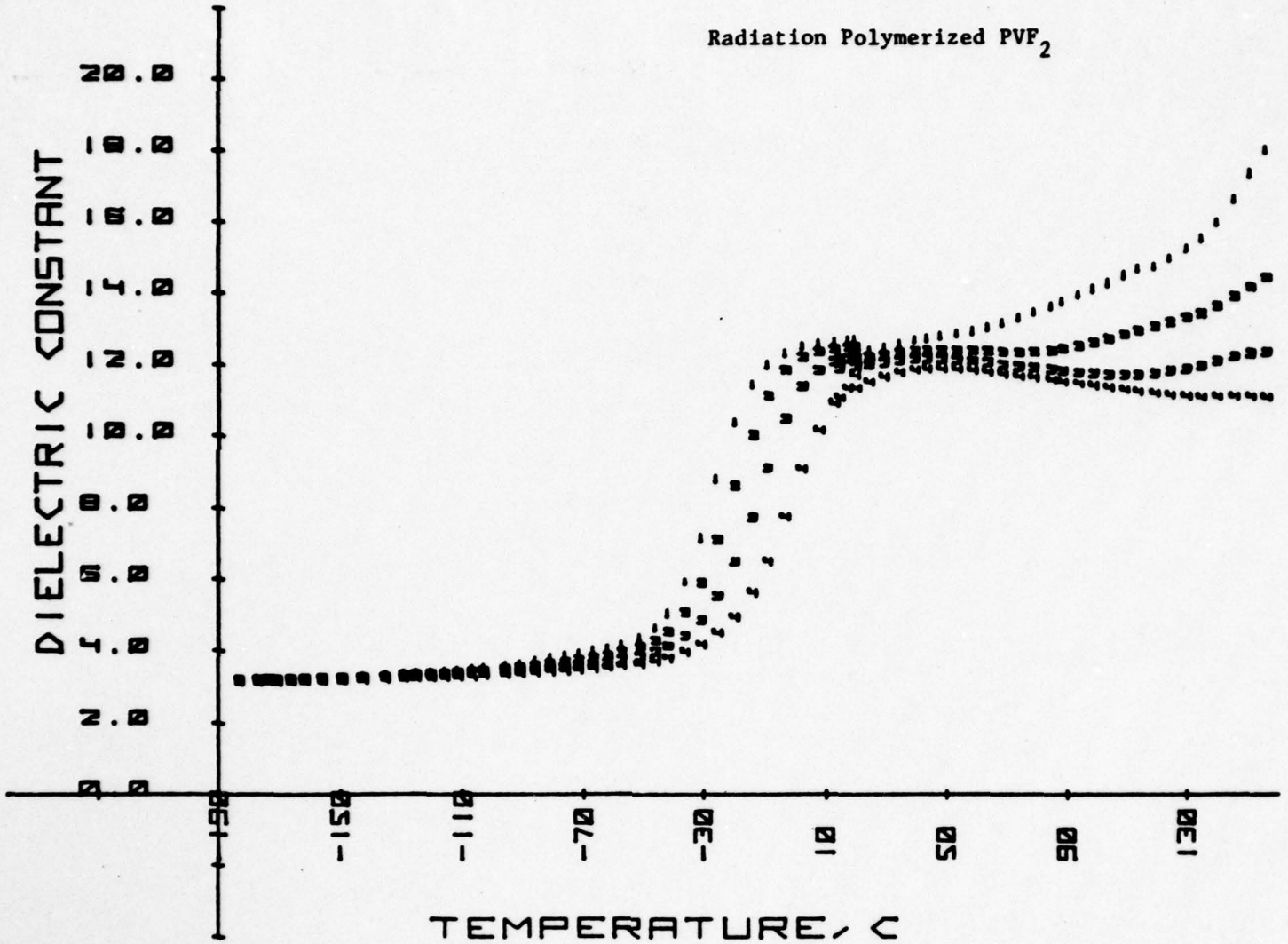

Radiation Polymerized PVF2
DIELECTRIC CONSTANT
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
-190
-150
-110
-70
-30
10
50
90
130
TEMPERATURE, C

Figure 9.

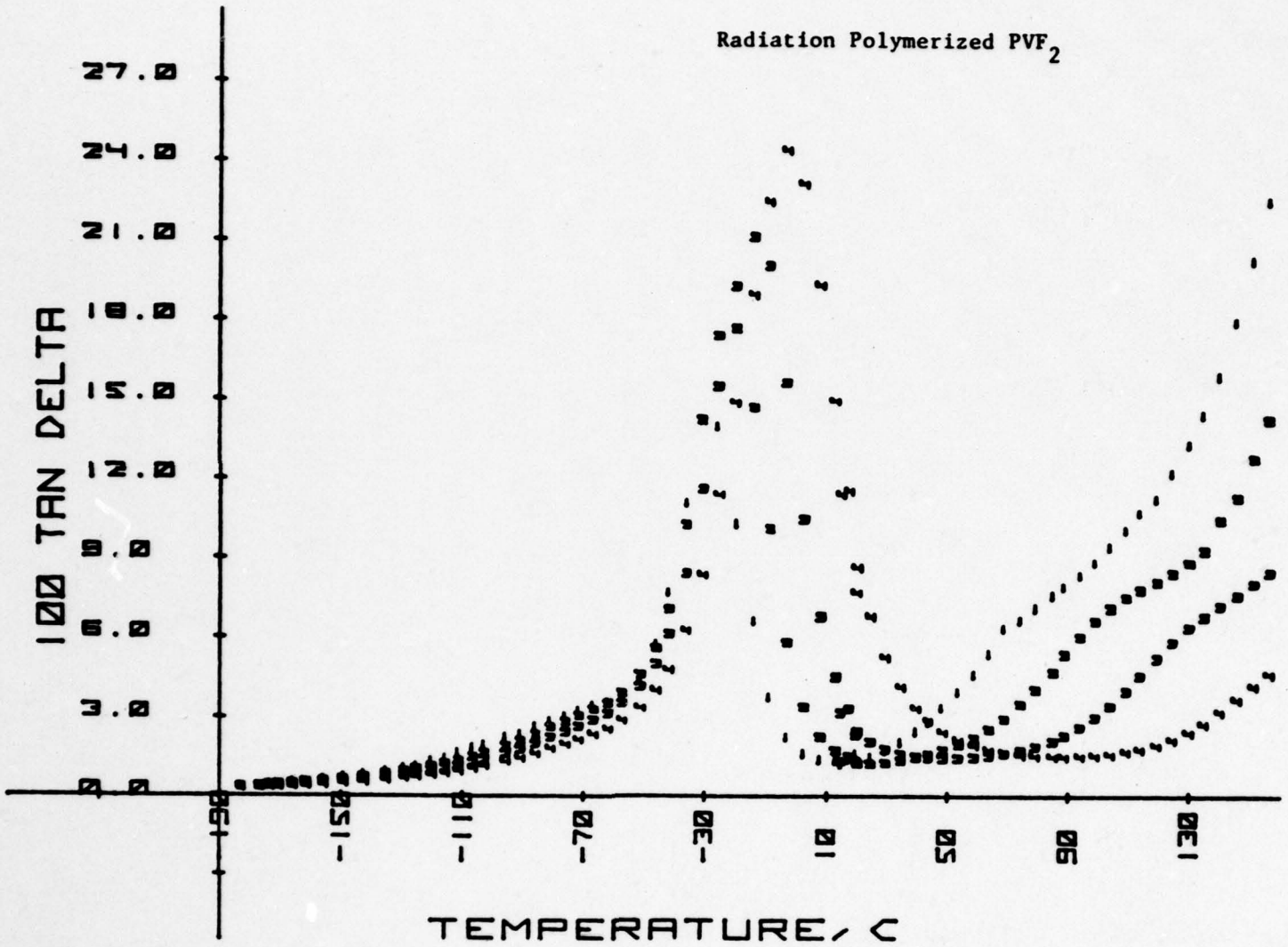

Radiation Polymerized PVF_2
100 TAN DELTA
27.0
24.0
21.0
18.0
15.0
12.0
9.0
6.0
3.0
0
-190
-150
-110
-70
-30
10
50
90
130
TEMPERATURE, C

Figure 10.

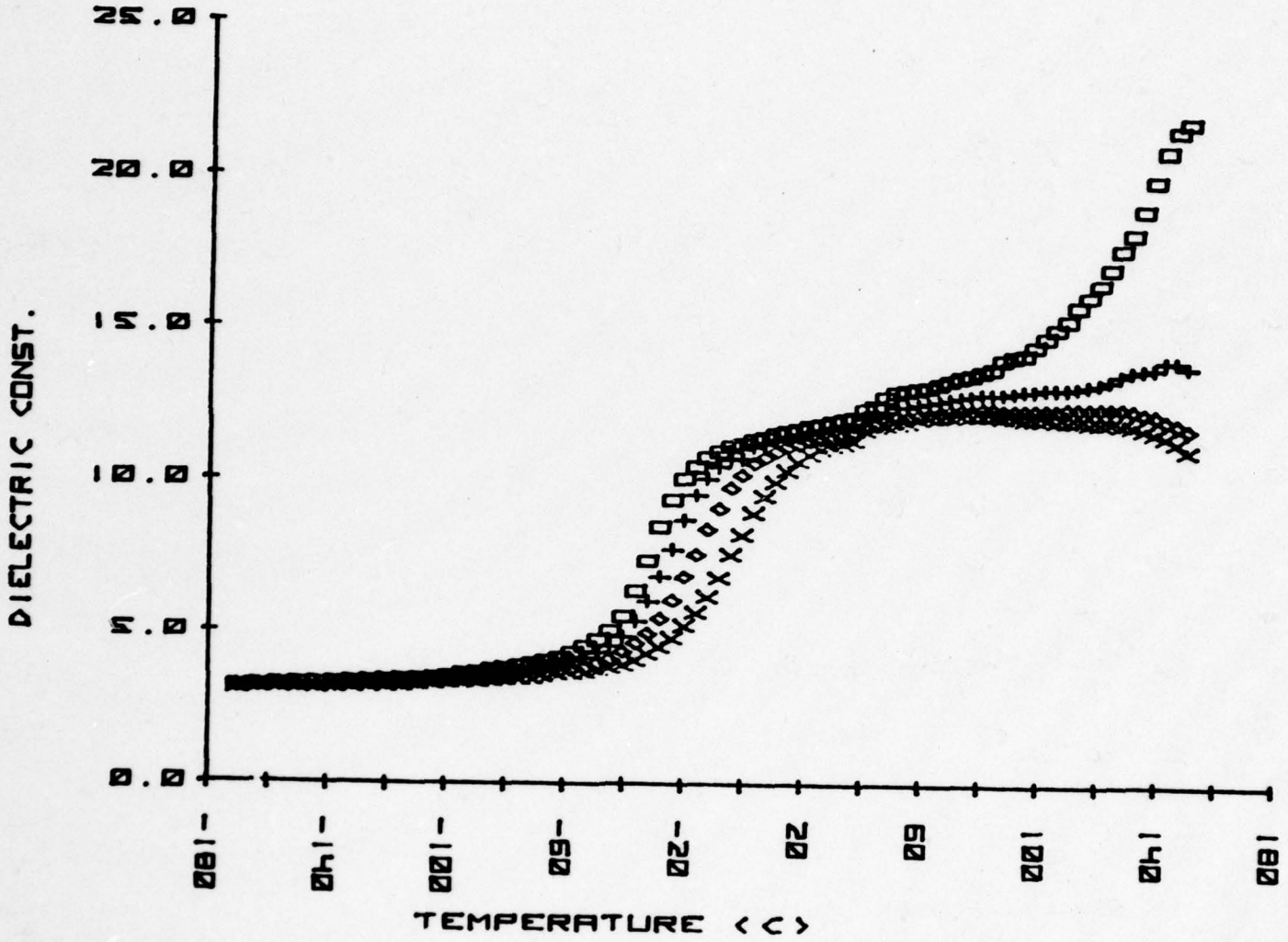

25.0
20.0
15.0
10.0
5.0
0.0
DIELECTRIC CONST.
-180
-140
-100
-60
-20
20
60
100
140
180
TEMPERATURE (C)

Figure 11.

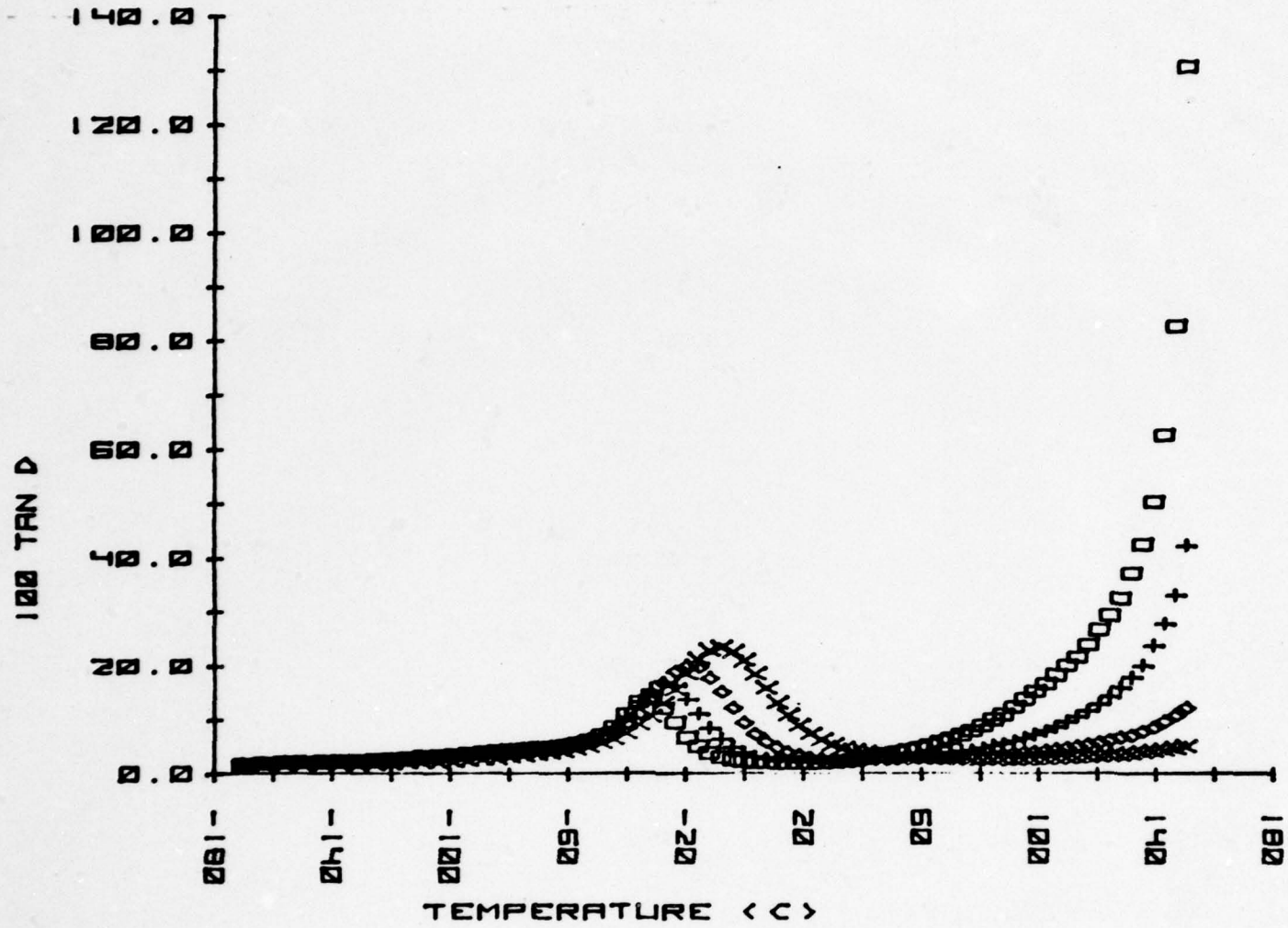

140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
100 TAN D
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20
40
60
80
100
120
140
160
180
TEMPERATURE (C)

Figure 12.

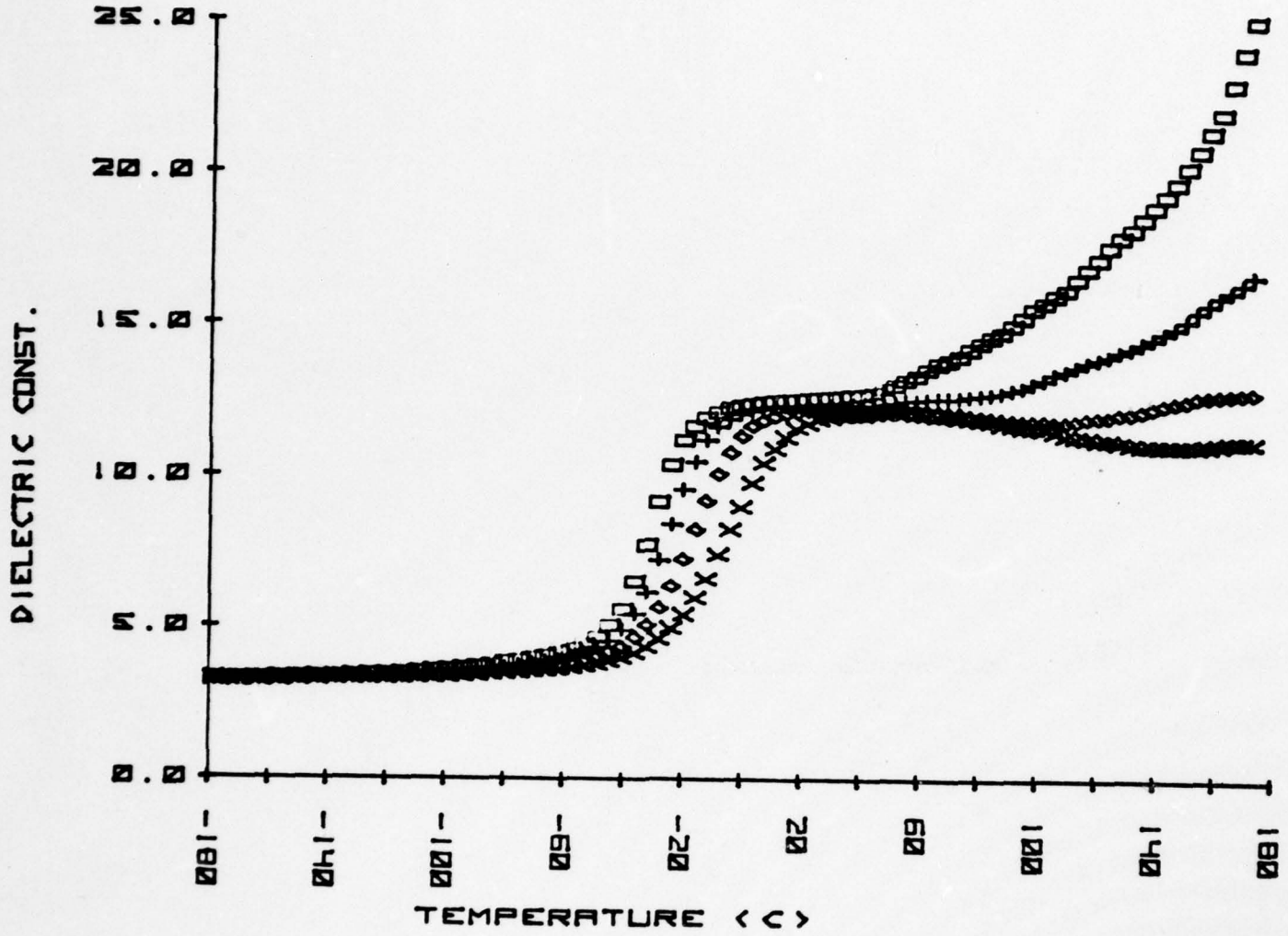

25.0
20.0
15.0
10.0
5.0
0.0
DIELECTRIC CONST.
-180
-140
-100
-60
-20
20
60
100
140
180
TEMPERATURE (C)

Figure 13.

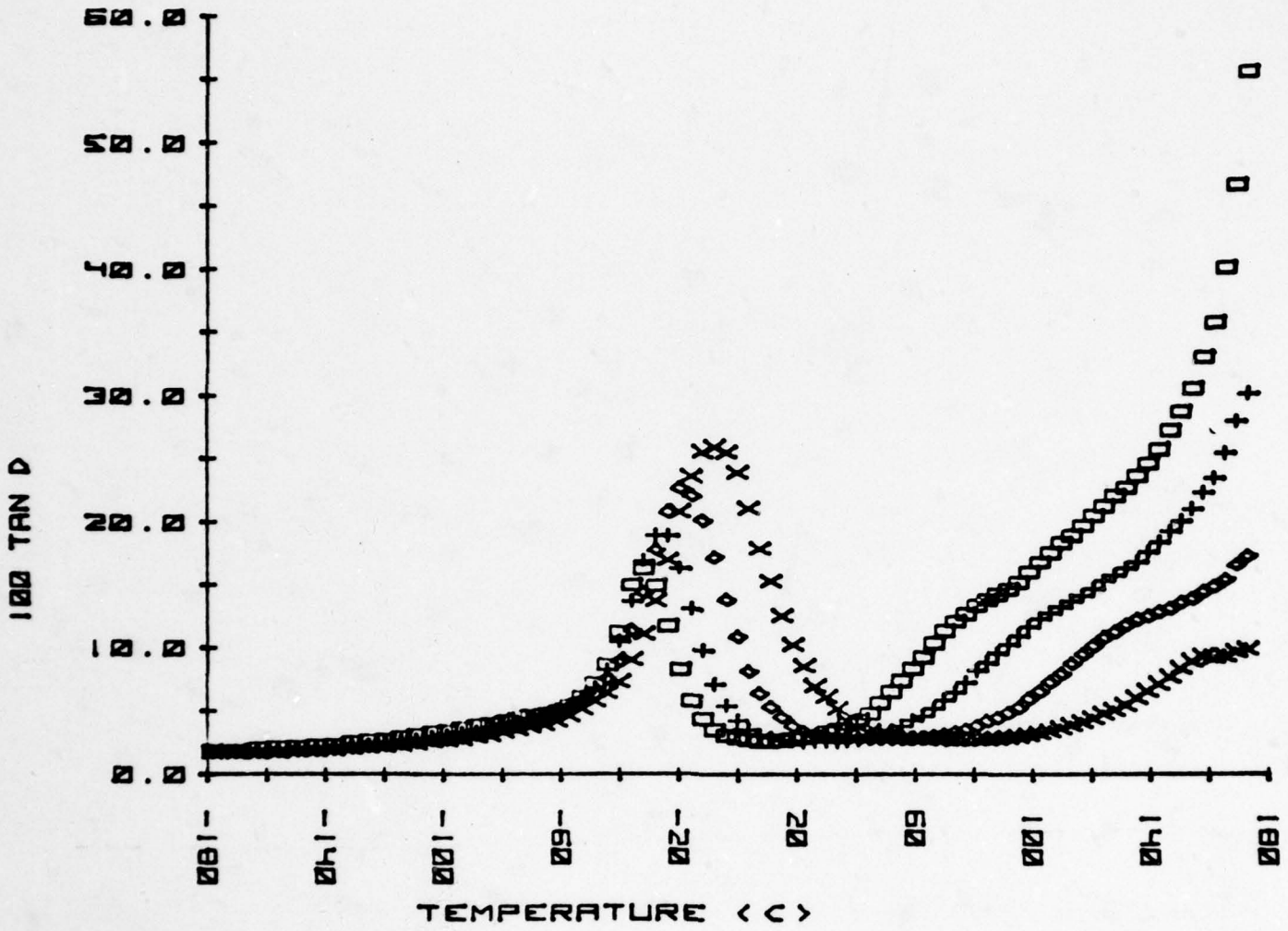

60.0
50.0
40.0
30.0
20.0
10.0
0.0
100 TAN D
-180
-140
-100
-60
-20
20
60
100
140
180
TEMPERATURE (C)

Figure 14.

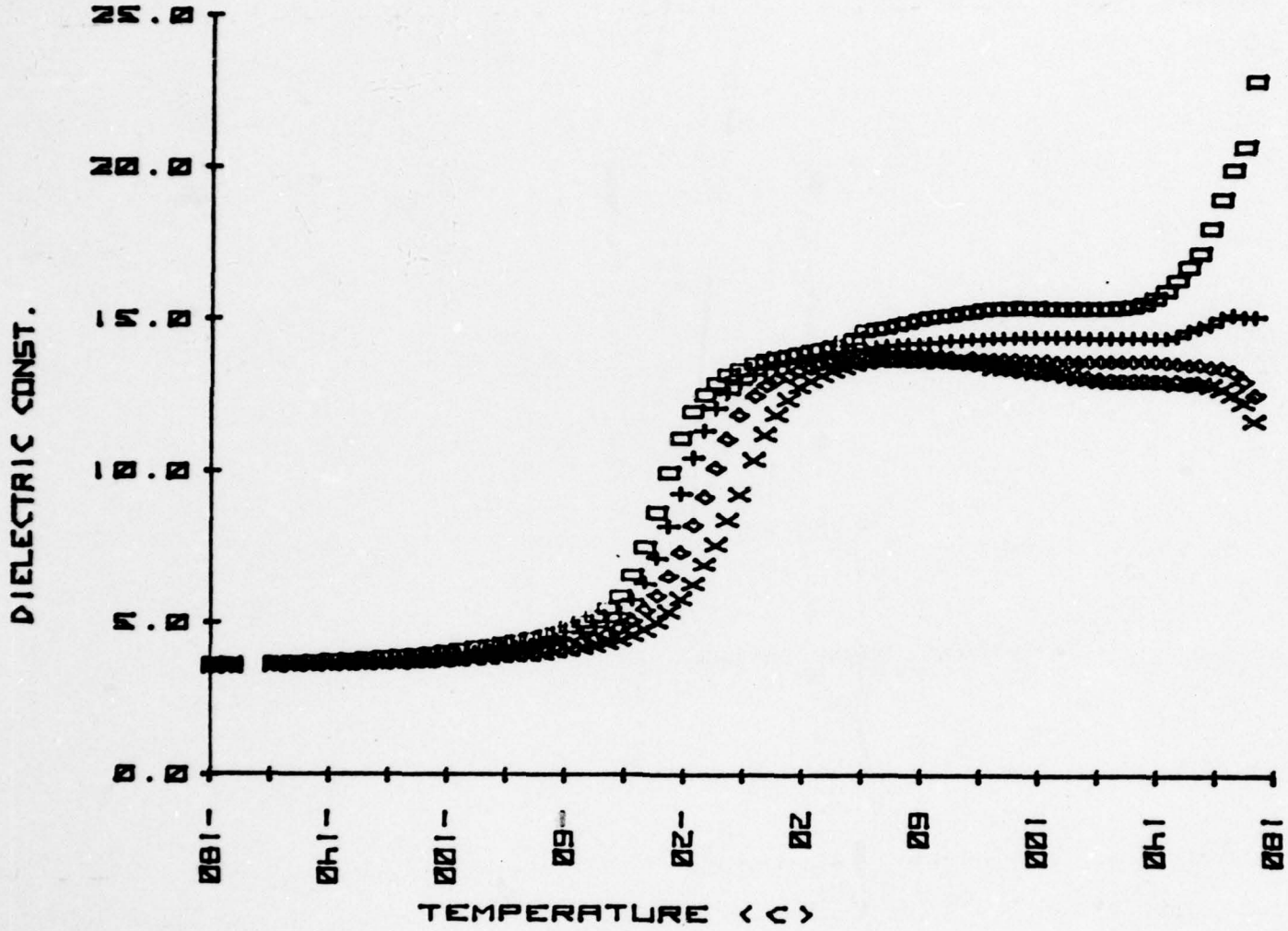

DIELECTRIC CONST.
25.0
20.0
15.0
10.0
5.0
0.0
-180
-140
-100
-60
-20
20
60
100
140
180
TEMPERATURE (C)

Figure 15.

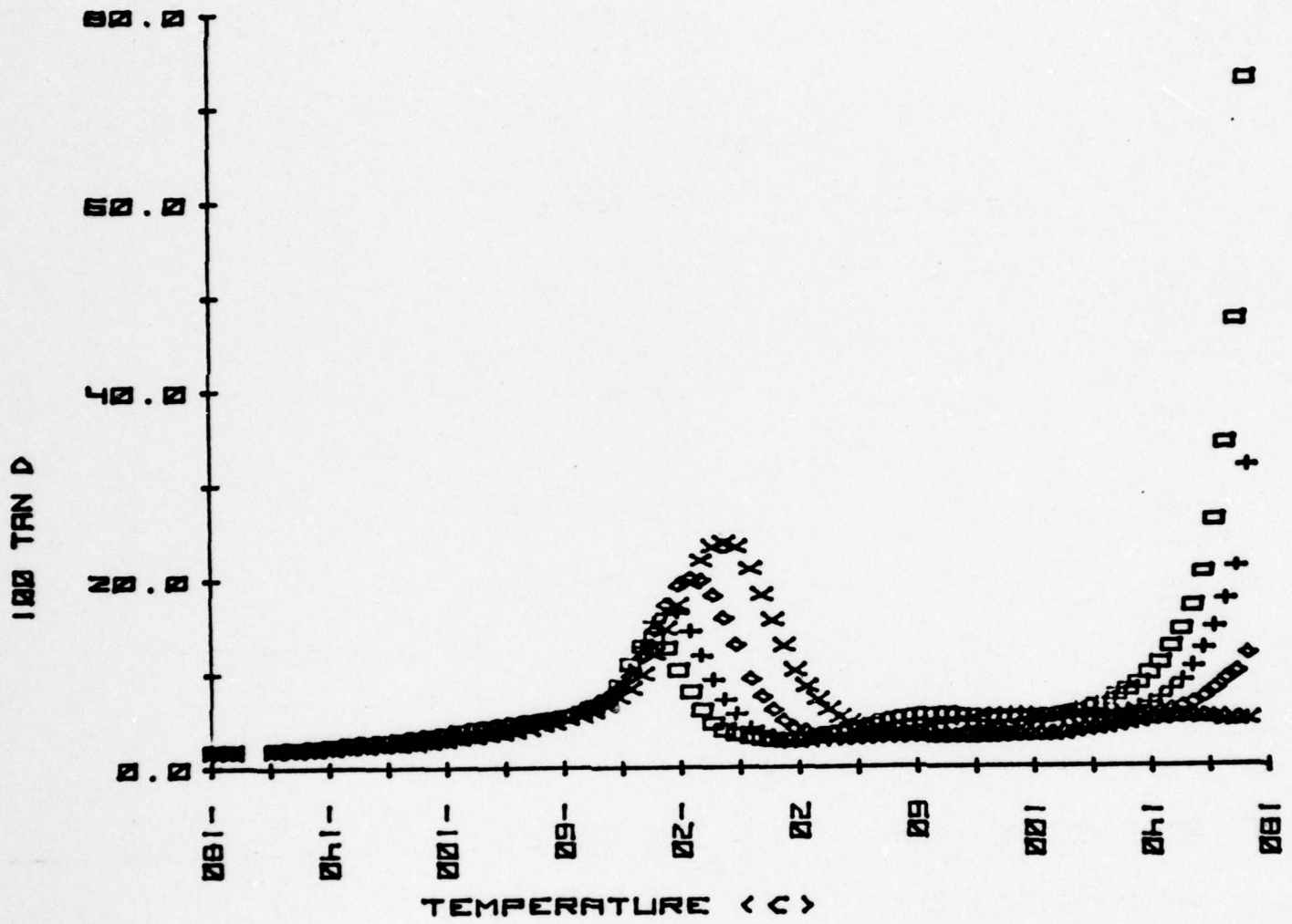

80.0
60.0
40.0
20.0
0.0
100 TAN D
-180
-140
-100
-60
-20
20
60
100
140
180
TEMPERATURE (C)

Figure 16.

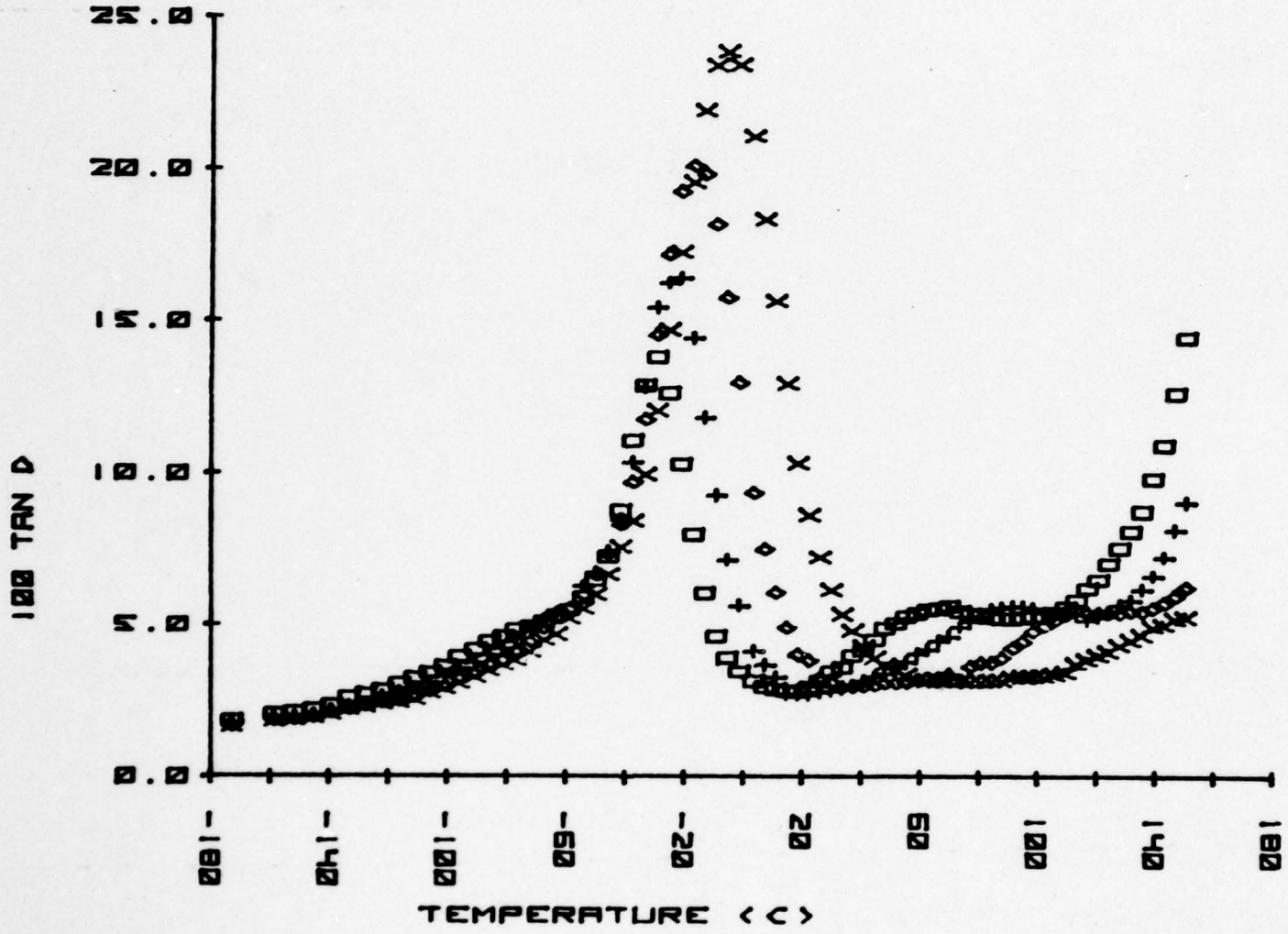

25.0
20.0
15.0
10.0
5.0
0.0
100 TAN D
-100
-75
-50
-25
0
25
50
75
100
TEMPERATURE (C)

Figure 17.

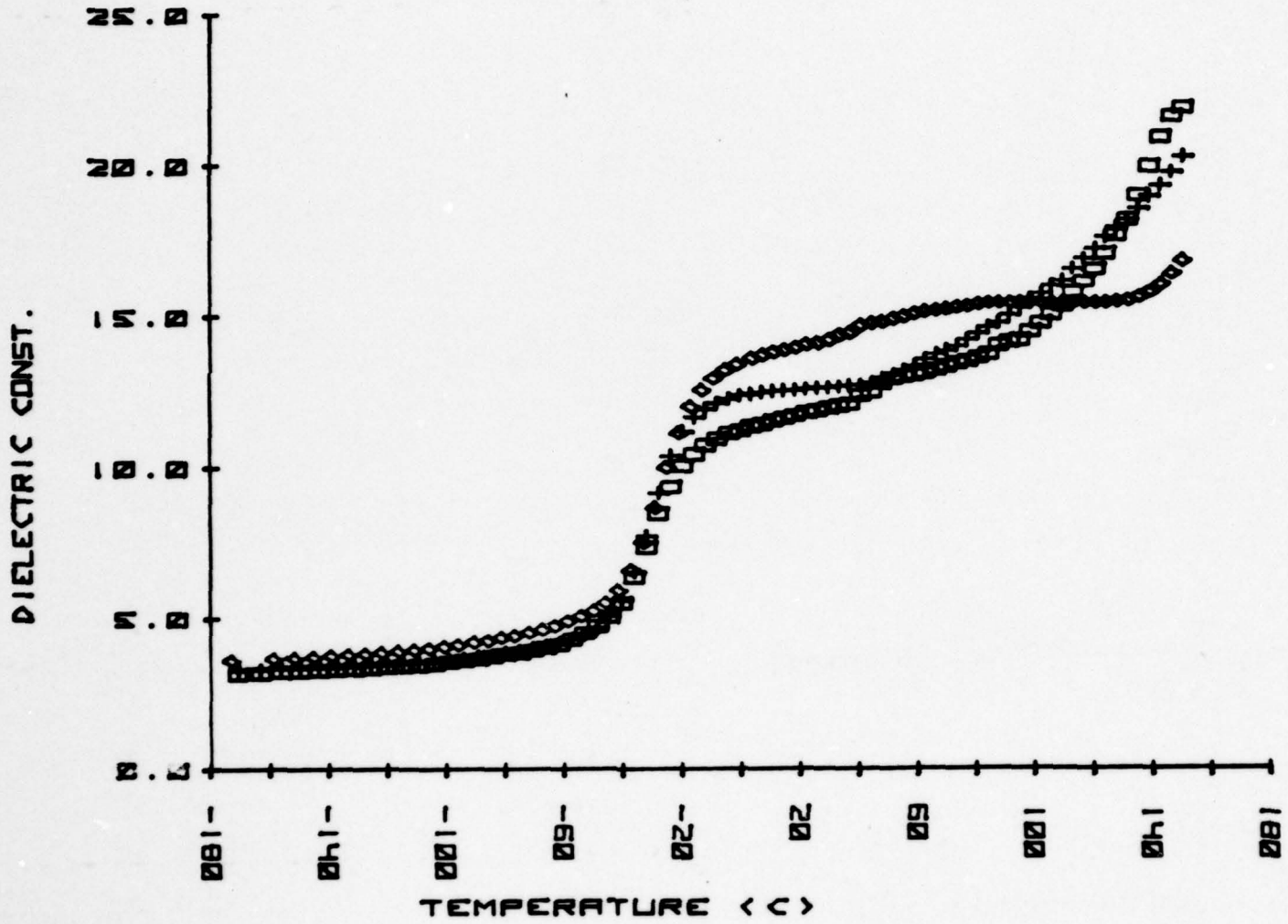

DIELECTRIC CONST.
25.0
20.0
15.0
10.0
5.0
0.1
-180
-140
-100
-60
-20
20
60
100
140
180
TEMPERATURE (C)

Figure 18.

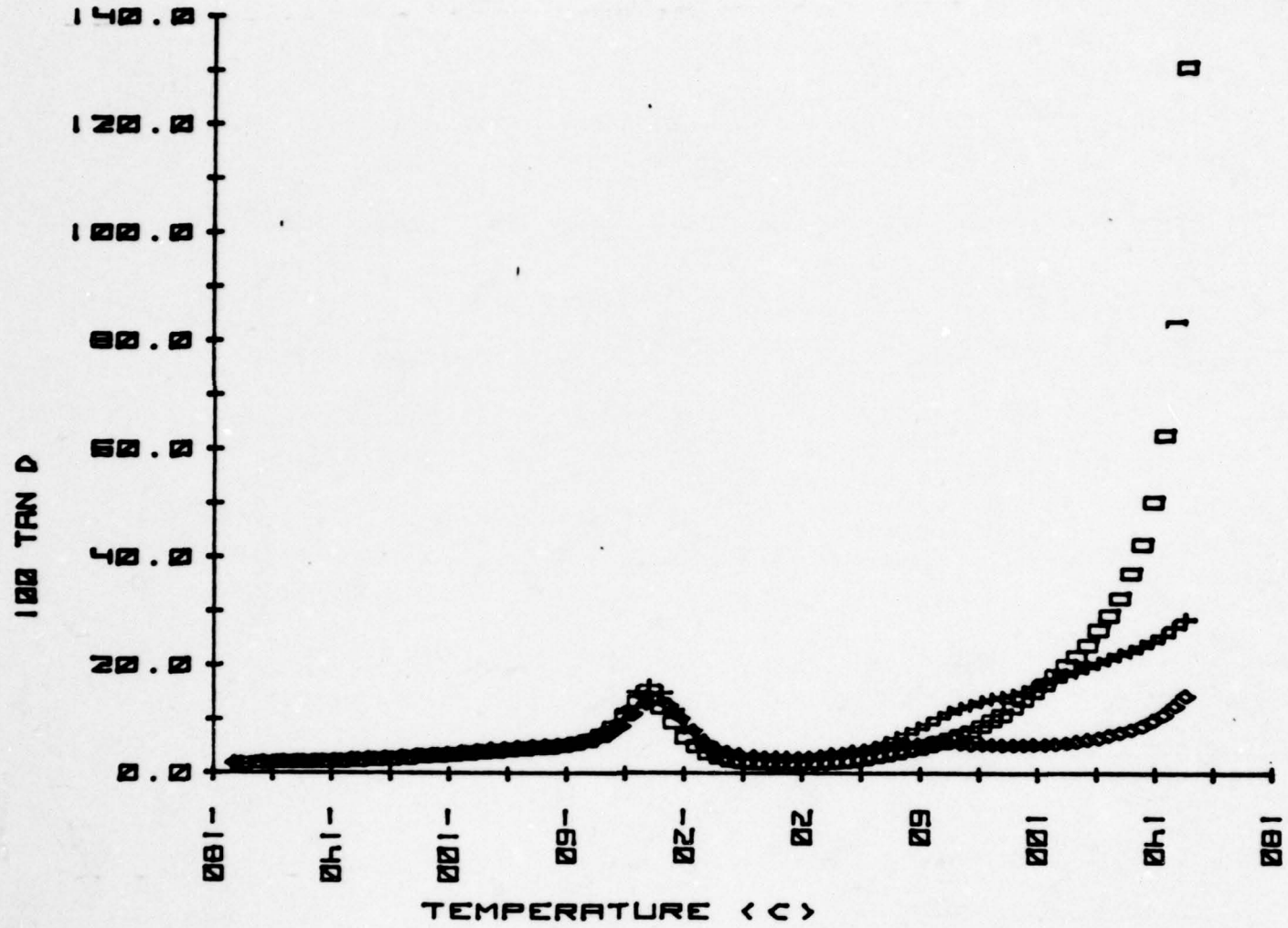

140.0
120.0
100.0
80.0
60.0
40.0
20.0
0.0
100 TAN D
-180
-140
-100
-60
-20
20
60
100
140
180
TEMPERATURE (C)

Figure 19.

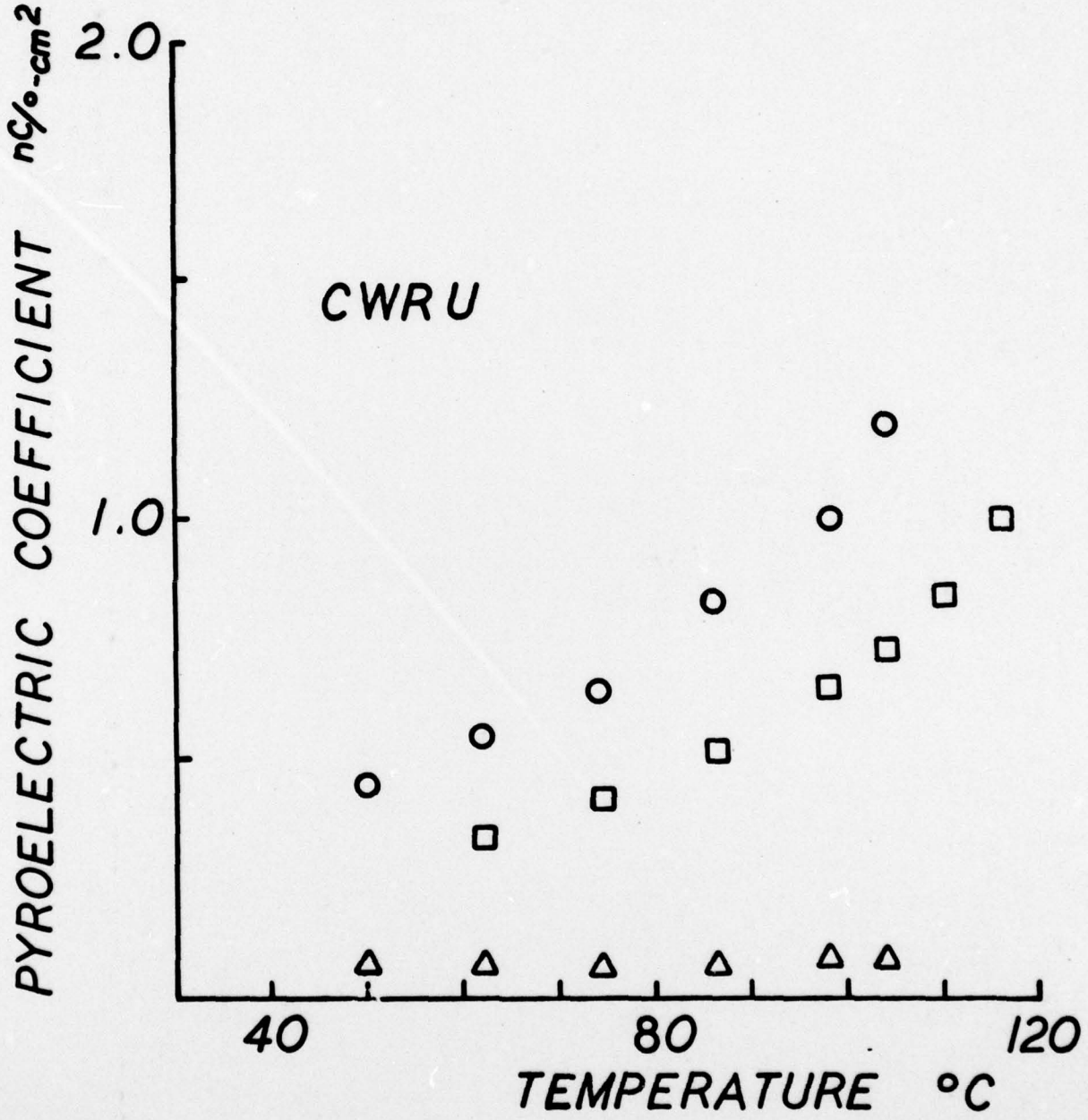

PYROELECTRIC COEFFICIENT nC/°-cm²
2.0
1.0
CWRU
40
80
120
TEMPERATURE °C

Figure 20.

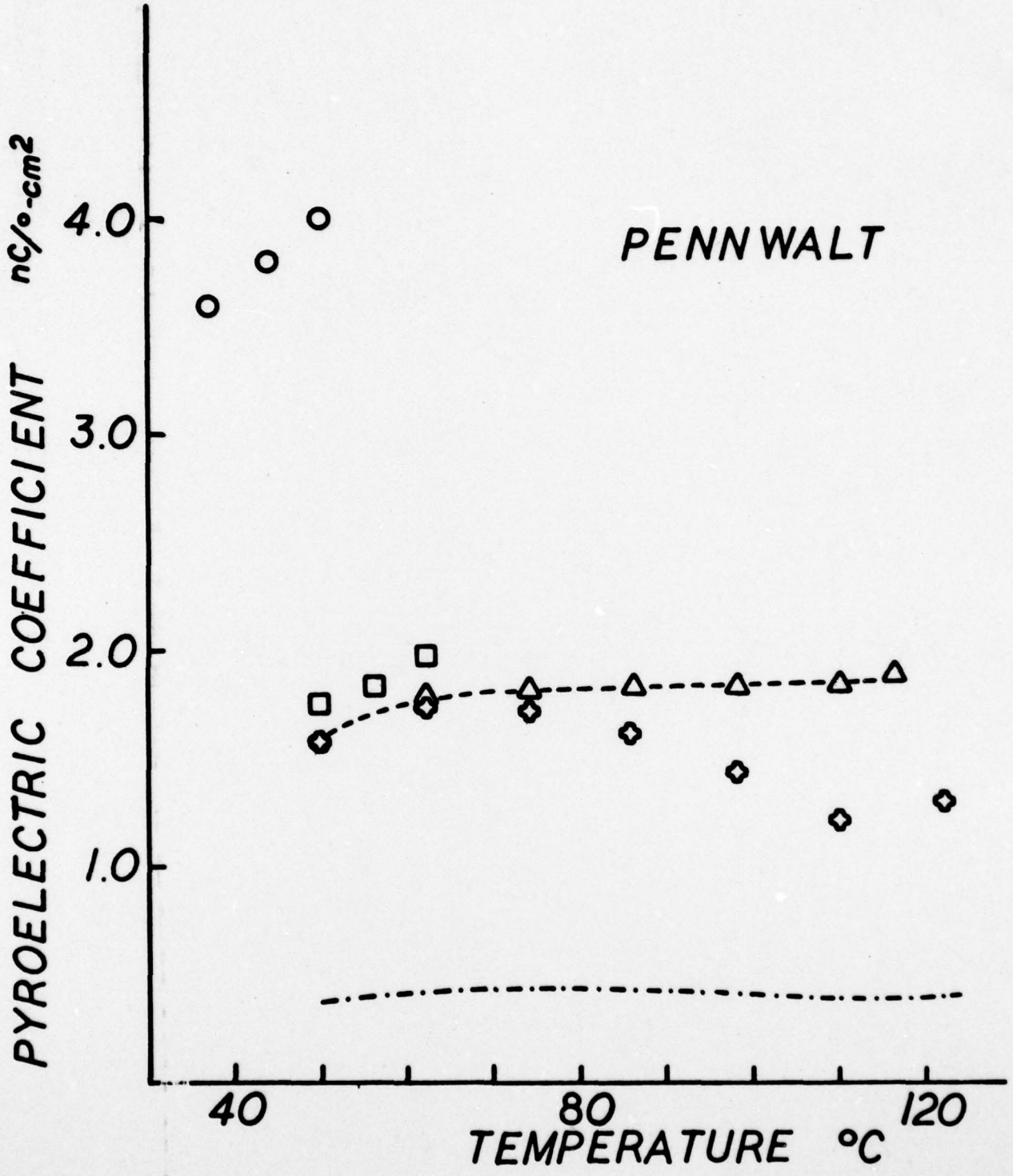

PENNWALT
PYROELECTRIC COEFFICIENT nC/°-cm²
4.0
3.0
2.0
1.0
40
80
120
TEMPERATURE °C

Figure 21.

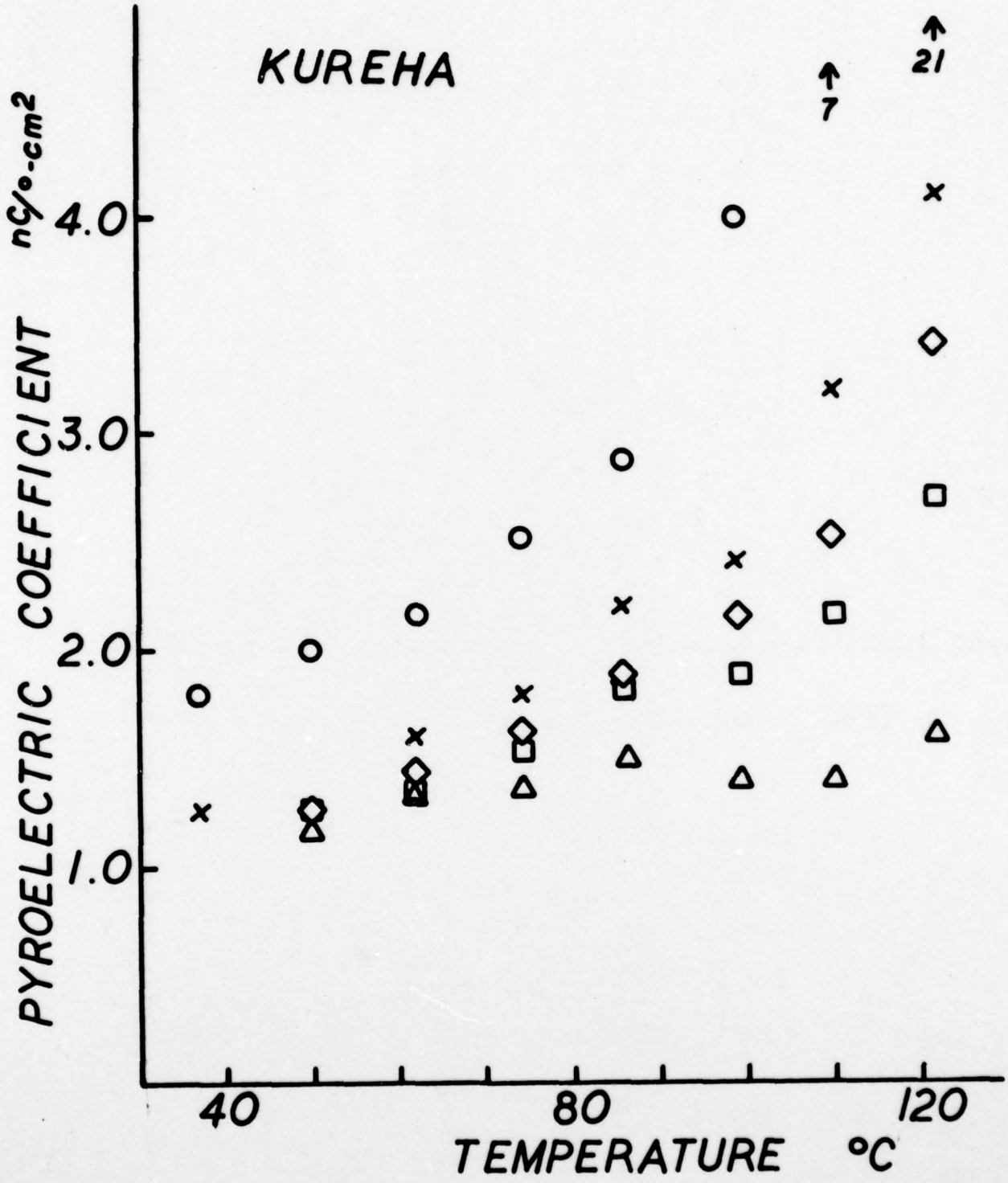

KUREHA
PYROELECTRIC COEFFICIENT nC/°-cm²
4.0
3.0
2.0
1.0
7
21
40
80
120
TEMPERATURE °C

Figure 22.

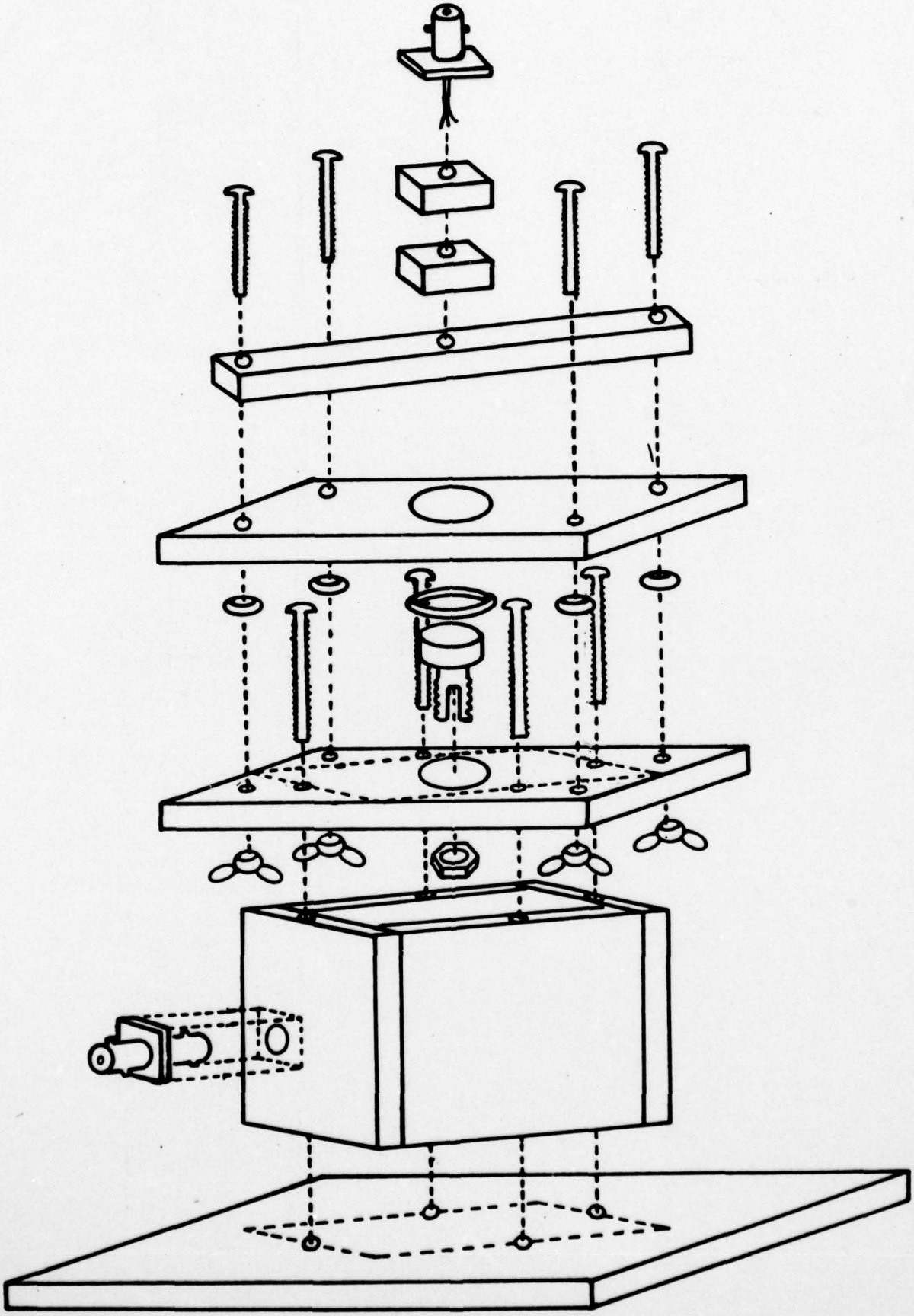


Figure 23.